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# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT

# LEIDEN.

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

OF THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

**N°. 97—108.**

SUPPLEMENT N°. 15–19.

DECEMBER 1906–AUGUST 1908.

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19. Corrigenda and Addenda (with three plates). May 1908.

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For insertion in the Volume N°. **97–108**.

## Erratum Communication N°. 100 b.

title-page l. 1 from the bottom: for “420—430”
read “418—420”.

## Erratum Communication N°. 101 a.

p. 9 l. 18 from the top: for “94 *f*” read “95 *f*.”

## Erratum Communication N°. 102 a.

p. 8 l. 13 from the bottom: for 282.75” read „182.75”.

## Erratum Communication N°. 102 b.

p. 15 l. 11 from the bottom: for “100*a*” read “101*b*.”

## Errata Communication N°. 102 c.

title-page l. 1 from the bottom: for “741—742”
read “815—816”.
p. 20 l. 11 from the bottom: for “52.797” read “59.797”.

## Errata Communication N°. 102 d.

title-page l. 5 from the bottom: for “wit hthis”
read “with his”
l. 1 „ „ „ for „743—744”
read “817 –818”.

## Erratum Supplement N⁰. 16.

title-page l. 1 from the bottom: for “243—245” read “233—242”.

## Erratum Supplement N⁰. 17.

p. 4 l. 6 from the bottom: for “188” read „183”.

## Erratum Supplement N⁰. 19.

p. 17 l. 16 from the top: for “supplement” read “communication”.

See further Supplement N⁰. 19.

# COMMUNICATIONS

FROM THE

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BY

PROF. DR. H. KAMERLINGH ONNES,
*Director of the Laboratory.*

## No. 97a.

**Dr. H. KAMERLINGH ONNES and C. BRAAK.** "Isotherms of diatomic gases and their binary mixtures. VI. Isotherms of hydrogen between — 104° C. and — 217° C." (*with two plates*).

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam,* **29 December 1906**, p. 517—539).

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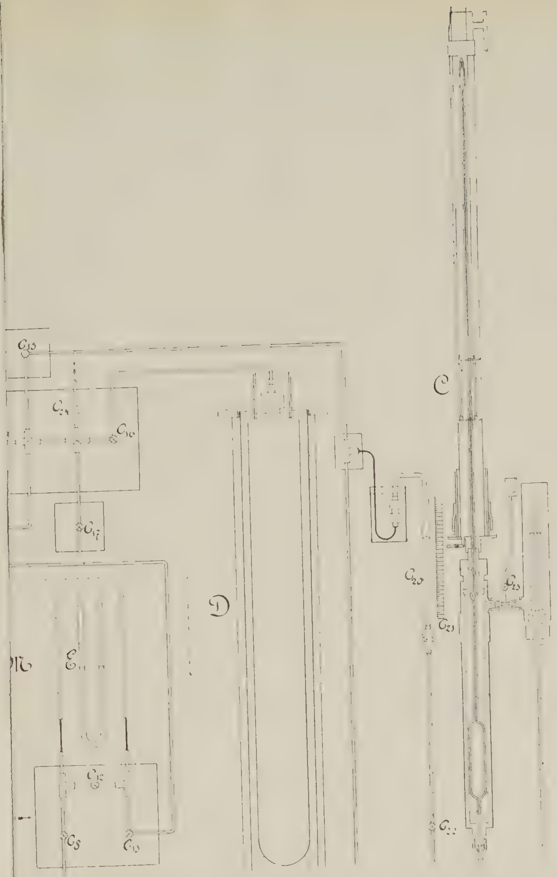
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**Dr. H. KAMERLINGH ONNES and C. BRAAK. Isotherms of diatomic gases and their binary mixtures. VI. Isotherms of hydrogen between — 104° C. and — 217° C.**

PLATE I.

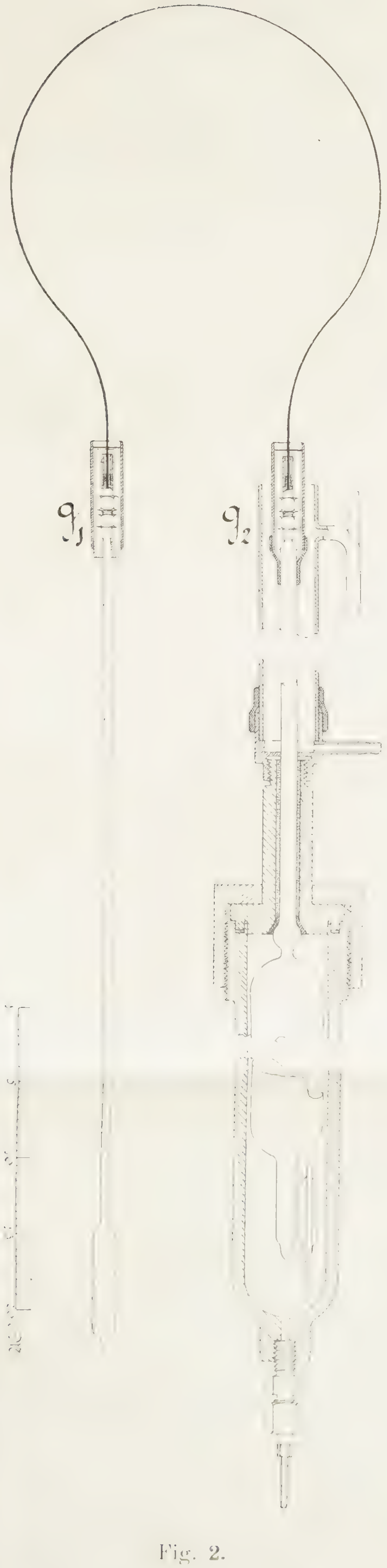


Fig. 2.

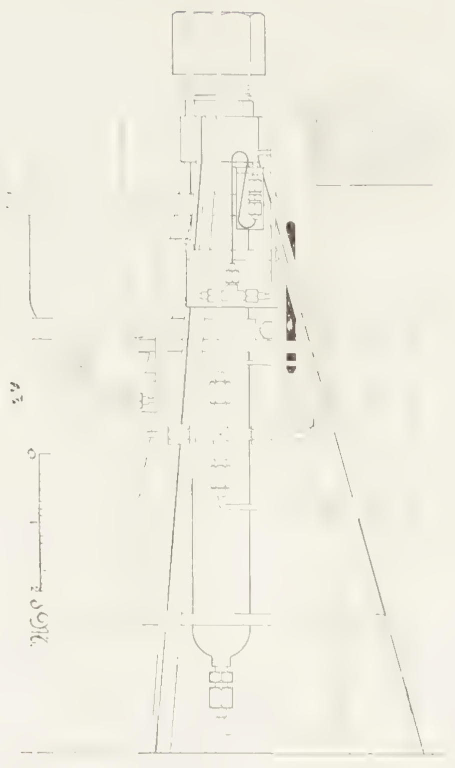


Fig. 3.

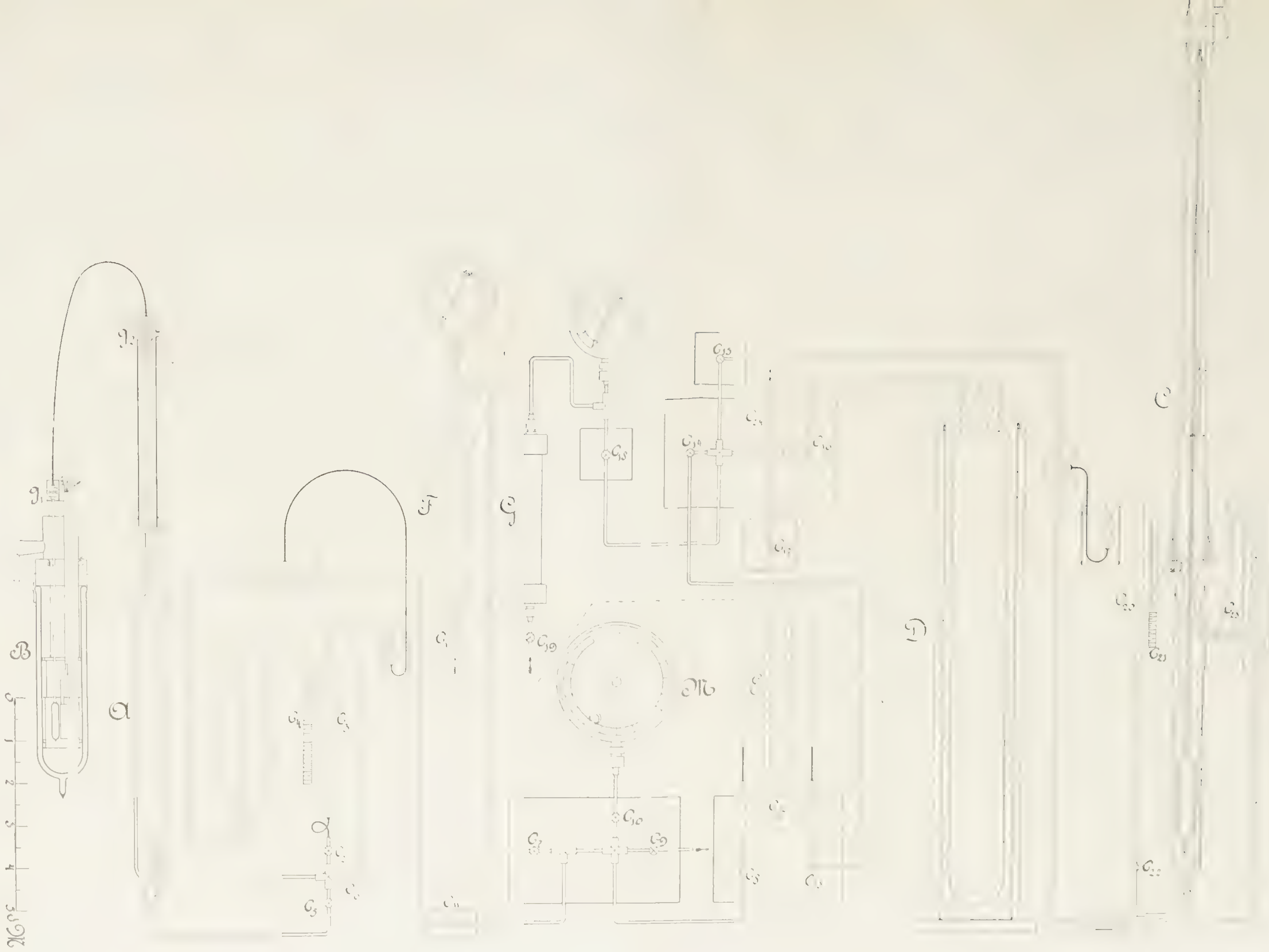


Fig. 1.

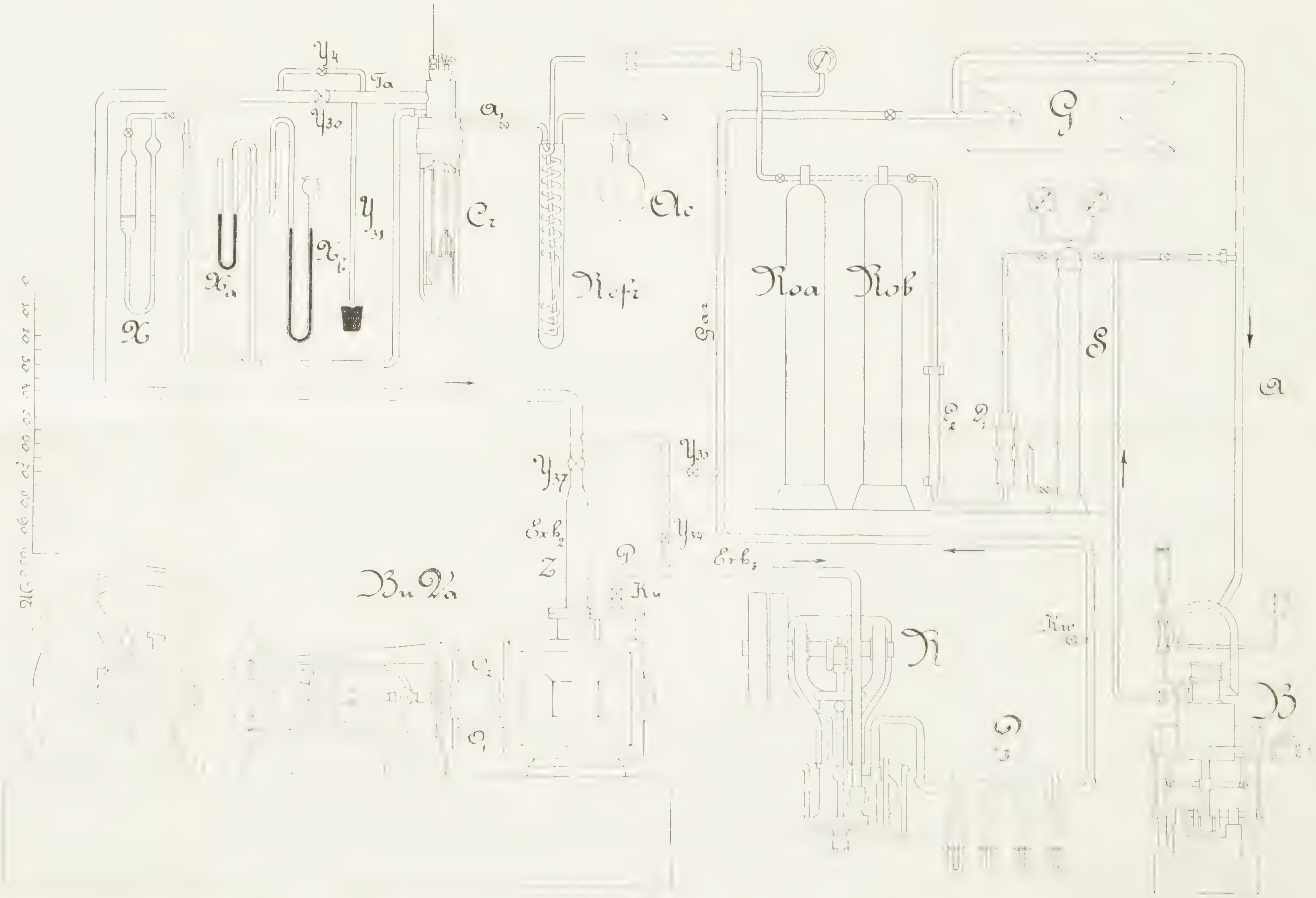


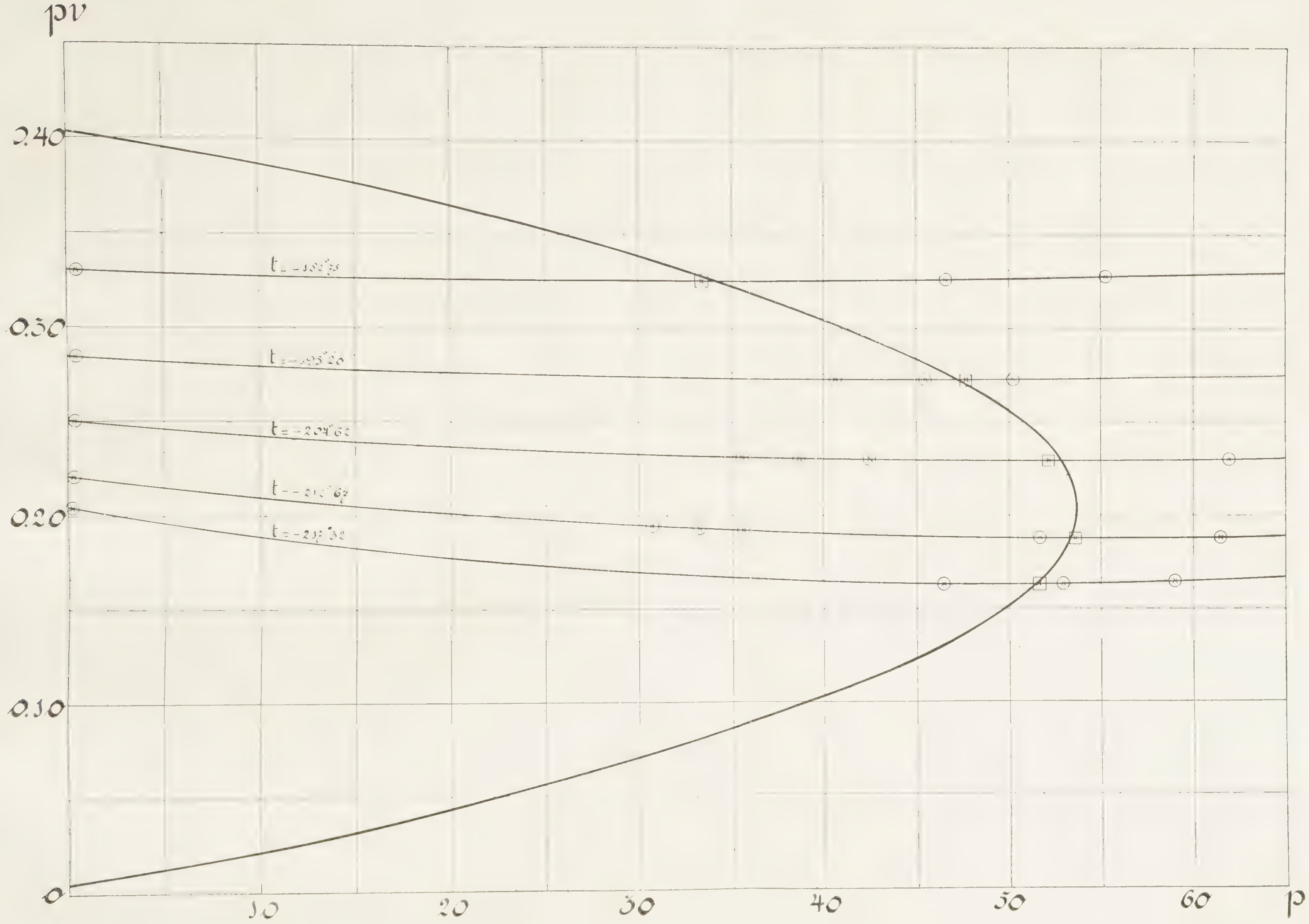
Fig. 4.

Communication No. 97ª.

Dr. H.

Dr. H. KAMERLINGH ONNES and C. BRAAK. Isotherms of diatomic gases and their binary mixtures. VI. Isotherms of hydrogen between —104° C. and —217° C.

PLATE II.



Communication N° 97^a

## **Dr. H. KAMERLINGH ONNES and C. BRAAK.** "*Isotherms of di-atomic gases and their binary mixtures.* VI. *Isotherms of hydrogen between* — 104° C. *and* — 217° C."

### § 1. *Introduction.*

The investigation treated in this Communication forms part of the investigation on the equation of state of hydrogen, which has been in progress at Leiden for many years. [1]

With that part of our measurements [2] which we now deem fit for publication, we have more directly carried on the work that H. H. Francis Hyndman had already done with one of us (K. O.) before 1904, so that, though all the observations, one for this, another for that reason, but always for the purpose of reaching the desired accuracy (which, we may add, was increased in the course of the investigation) have been repeated, an important share of the final success of the measurements is due to the said investigator.

The results obtained by us furnish data for reducing experimentally the readings of the hydrogen thermometer to the absolute scale (see the following communication), and for determining the deviation between the net of isotherms of hydrogen and that of the mean reduced equation of state (see Comm N$^{os}$. 71 and 74) [1] The points determined in the net of isotherms are only few in number, but these few points have been determined with particular care, so that, so to say, they form normal places in the examined region of the equation of state, with which without preliminary adjustment we may set about the calculation of individual virial coefficients. Characteristic of them is that every group of such normal places obtained by determinations with the piezometer and manometer (see Comm. N$^{os}$ 69 and 78) lies really on the same isotherm (that of about — 104°, — 136°, — 183°, — 195°, — 205°, — 213° and —217°), and that on these same isotherms every time a point has been obtained at small density by a determination with the hydrogen thermometer (see Comm. N$^0$. 95*e*). The great difficulty [2] of this investigation lies in obtaining the required constancy and stability of the low temperatures. Accordingly the arrangement of reliable cryostats was made a separate subject of investigation at Leiden (cf. Comm. N$^{os}$. 83 and 94).

---

[1] In Comm. N°. 69, where the apparatus have been described which were used in this investigation, the previous Communications referring to this subject, have been mentioned. Since then the isotherm for 20° C. to 60 atms. was given in Comm. N°. 70 with the accuracy of which the open standardmanometer (Comm. N°. 44) and the closed standard manometers (Comm. N°. 50) admit. This Communication is joined by Comm. N°. 78 for the determination of the isotherms of hydrogen at 20° C. and at 0° C. with the apparatus that have also been used for this investigation. The suitability of these apparatus for accurate determinations of isotherms has been shown in Comm. N°. 78, and is confirmed by this Communication for low temperatures. Several communications e. g. Nos. 83, 84, 94*b*, and 94*f*, further 85 and 95*b*, finally Nos. 89, 93, and 95 are more or less in connection with this investigation, the great importance of which, if accurately carried out, is demonstrated in Suppl. N°. 9.

[2] We soon hope to publish the results of measurements at higher pressures and lower temperatures, and also those of supplementary determinations at lower pressures.

This investigation comprises three series of piezometer-determinations at densities respectively about 70, 160, and 300 times the normal one [3]. Several of the observations mentioned here lie in the neighbourhood of the curve of the minima of $p\,v$. They enable us to determine the shape of this curve pretty accurately (see § 13).

We confine ourselves in this communication to our observations themselves. A discussion of them, also in connection with the results of other observers will be given in a following communication.

---

[1] Definitive values for the virial coefficients $B$ and $C$ (§ 12 contains only provisional values), from which the difference with those according to the reduced equation may follow, are given in the following communication.

[2] WITKOWSKI, whose important investigation on the expansion of hydrogen (Bulletin de l'Académie des Sciences de Cracovie 1905) had already appeared before the experiments mentioned in this communication had been completed, already mentions this as an explanation for the fact, that he has dropped the direct determination of isotherms at temperatures lower than — 147°.

[3] The limits are chiefly given by the pressure under which the gas stands; they are about 20 and 60 atms.

§ 2. *Survey of the apparatus used*

*a.* On Pl. I in fig. 1 we find a schematic[1]) representation of the system of the measuring apparatus and the auxiliary arrangements, excepted those which serve for keeping constant the temperature in the cryostat. The compression apparatus $A$ is the same as that mentioned in Comm. N⁰. 84. For the meaning of the system of tubes, cocks and other parts we may refer to Comms. N⁰. 69 and N⁰. 84. The same letters have been used, except that in this communication $c_1$ is used for the cock which admits the compressed air, and $c_2$ for the cock which shuts off the level glass. Of the compression tube, provided with the system of cocks, mercury-reservoir and level-glass belonging to it a front-view is given in fig. 3 of Pl. I. The piezometer with the connections $g_1$ and $g_2$ has been represented in detail in fig 2 of Pl. I.

The arrangement of the cryostat $B$ which has served for the determinations mentioned in this communication, is described in Comm. N⁰. 94*d*.

For the description of the apparatus serving for keeping the temperature in the cryostat constant, we may also refer to this last communication. Fig. 4 of Pl. I may also serve for elucidating this description for the special case that our piezometer is placed in the cryostat.

The pressure is conveyed (see fig. 1, Pl. I) from the compressiontube to the manometer along $c_{11}$, $c_8$, $c_{12}$, $c_{13}$, $c_{14}$, and $c_{15}$. By closing and opening $c_{12}$ the differential-manometer $E$[2]) may be shunted in and out. By means of the cocks $c_8$ and $c_{13}$ it may be shut off from the rest of the pressure-conduit, when great differences in pressure are brought about, or are to be feared [1]) [2]). The apparatus are placed in two rooms as has been indicated in the figure by a dotted line. By closing one of the cocks $c_{13}$ and $c_{14}$ the two parts may be treated as independent systems. This was done when the manometer was compared with the open manometer connected at $c_{17}$. The manometer $C$ is the same as served for the investigations of Comm. N⁰. 78. The reservoir $D$ serves, if necessary, for eliminating the injurious influence of small leaks, for which purpose it is placed in ice. At $c_{16}$ it can be coupled to the system. In the experiments of this communication there was no need to use it [3]). The pressure is exerted by compressed air, which enters through $c_1$ and $c_{19}$ along the drying tubes $F$ and $G$; and is regulated by blowing off along $c_{24}$. The cocks $c_{15}$, $c_{18}$, $c_{20}$, $c_{21}$, $c_{22}$, and $c_{23}$ have analagous meaning to $c_{11}$, $c_7$, $c_3$, $c_4$, $c_5$ and $c_6$.

---

[1]) The individual apparatus are represented on the same scale, the connections schematically.

[2]) This manometer, which was formerly used with the open standard-manometer (see $C$ fig. 1 Comm. N⁰. 44) and had now been removed to the piezometer, was of great use for finding leaks.

All couplings of the conducting tubes in which air is to be kept at constant pressure, have been placed (cf. the plate to Comm. N⁰. 94*b*) in trays filled with oil, according to what has been said in Comm. N⁰. 94*b*.

*b*. With regard to the means for keeping a constant temperature in the cryostat, the system of pumps and auxiliary arrangements for the regulation of the temperature, belonging to the circulation of oxygen, has been represented in fig. 4 of Pl. I. For a description we refer to Comm. N⁰. 94.

Some particulars about the ethylene circulation used for the determinations of Series I, are to be found in Comm. N⁰. 94*f* XIII § 1.

## § 3. *The manometer.*

The pressure-measurements were performed by means of the closed auxiliary manometer described in Comm. N⁰. 78*c*. As a comparison of this manometer made in 1904 with the standard manometer A IV (cf. Comm. N⁰. 78 § 17), yielded an unsatisfactory result, and led us to expect that the auxiliary manometer was no longer reliable, it was compared at four points with the open standard-manometer, to which the improvements mentioned in Comm. N⁰. 94*b* were applied [1]). The results of this comparison have been put together in the subjoined table.

---

[1]) A couple of mercury-receptacles, which served for receiving the mercury that might overflow, have not been represented in the figure.

[2]) The system which we have so far described and which belongs to the piezometer, is placed in one of the rooms of the laboratory, situated in the immediate neighbourhood of the cryogenic department. The remaining apparatus which chiefly belong to the manometer are erected in the room with the standard manometer.

[3]) The adjustment of trays of oil for the different couplings rendered the search for leakages so easy, that an injurious leak needed never to remain.

Column *C* like column *C* of table XVII of Comm. N⁰. 78*c* represents the reading of the pressure determined with the open manometer (Comm. N⁰. 44) Every value is the mean of two observations. Column *F* gives the pressure read by means of our closed auxiliary manometer. Each of the values has been obtained as a mean from three observations. In the calculation the calibration derived in Comm. N⁰. 78*c* has been used. In column *G* the difference of the columns *F* and *C* is represented, column *H* contains this same difference expressed in the numbers of column *C* as unity. The pressure given by the auxiliary manometer appears to be too high for all pressures observed. It was obvious to ascribe this to a too high value assumed for the normal volume [2])

If we take the mean of the values in column *H*, we find 0.00087. If we diminish the normal volume and so also the pressures by this part of the original amount, the differences represented in column *K* remain between the indications of the auxiliary manometer and the open standard-manometer. These differences, considerably smaller than those in table XVII of Comm. N⁰ 78*c*, remain within the limits of accuracy fixed for this investigation, and justify us to estimate the mean error in the pressure measurements at $\pm \frac{1}{3000}$.

In the following the pressures have been calculated with this new value of the normal volume.

---

[1]) In the investigations with this manometer of Comm. N⁰. 70 the total absence of leaks was rare; here, however, it was easily brought about. Also the improved coupling of the steel-capillaries to the glass-capillaries of the open manometer by platinizing proved satisfactory. (See Comm. N⁰. 94*b*).

[2]) In connection with this diminution of the normal volume see also Comm. N⁰. 95*e*, § 11.

TABLE I. Manometer.

| C | F | G | H | K |
|---|---|---|---|---|
| 24.247 | 24.264 | + 0.017 | 0.00070 | — 0.00017 |
| 36.290 | 36.333 | + 0.043 | 0.00120 | + 0.00033 |
| 47.960 | 48.004 | + 0.044 | 0.00092 | + 0.00005 |
| 60.022 | 60.061 | + 0.039 | 0.00065 | — 0.00023 |

§ 4. *The piezometers and auxiliary apparatus.*

The piezometer used in the first series for the observations at a density 70 and the temperatures — 104°, — 136°, — 183°, — 195°, was of about the same dimensions as that used for the observations of Comm. N$^0$. 78. In the subjoined table, just as in the corresponding table II of that communication, the dimensions are given to facilitate a survey of the amount and the influence of the many corrections. The volumes are reduced to 17° C

TABLE II. Data $H_2$, Series I.

$U_1 = 6.4110$ cm$^3$ $\beta_1 = 5.0 \cdot 10^{-6}$ [1])

$U_2 = 0.0530$ » $\beta_4 = 4.7 \cdot 10^{-6}$

$V_3 = U_3 = 1.198$ »

$V_4 = 6.0174$ »

$U_4$ has been determined from a calibration table

$V_5 = 576.077$ cm$^3$

$v' = 0.722$ » per cm.

The stem $b_4$ (see Pl. II Comm. N$^0$. 69), on which the volume $U_4$ is read, was 30 cm long in order to enable us to determine every time three points on the isotherm which did not lie too near each other[1]. In others of our piezometers it was taken still longer.

---

[1]) The values of $\beta$ given here have been determined for the ordinary temperature and those for lower temperatures have been put equal to them. We hope soon to determine $\beta$ also for lower temperatures.

For the series II and III a piezometer of larger dimensions was used.

The necessity of the use of a larger gas-volume for determinations at densities higher than 120 times the normal one has already been mentioned in § 19 of Comm. N$^0$. 84. The volumenometer described there was not used, but just as in Series I the normal-volume was determined in the piezometer itself.

As in the preceding table the dimensions of the piezometer are given here.

TABLE III. Data $H_2$, Series III.

$U_1 = 5.1583$ $cm^3$.

$U_2 = 0.0382$ »

$V_3 = U_3 = 1.407$ »

$V_4 = 10.9645$ »

$U_4 =$ (see preceding table)

$V_5 = 2063.30$ $cm^3$.

$v' = 1.617$ » per cm.

$\beta_1 = 3.7 \cdot 10^{-6}$

$\beta_4 = 4.7 \cdot 10^{-6}$

In Series II the piezometer-reservoir had a volume of 10.343 $cM^3$., but for the rest the dimensions were the same as in Table III.

To detect any escaping of gas during the measurements at high pressure in consequence of leakages at the connections $g_2$ and $g_3$ (See Pl. II Comm. N$^0$. 69), cylindric glas oil-trays were placed round these couplings (see Pl. I fig 2) which enabled us to discover immediately even the slightest leakage; every where the oil-trays rendered excellent services, but here they were of the greatest importance for obtaining reliable results [1]).

---

[1] They may serve, inter alia, to give us information about the curvature and the inclination of the isotherms at the middle point.

### § 5. *The hydrogen*

The filling was accomplished for Series III with all the improvements described in Comm. N⁰. 94*e* § 2. For the first series the purification by means of cooling in liquid air was not yet applied, in the second series it was, but without application of high pressure.

### § 6. *The temperatures.*

The temperatures $t_4$ and $t_3$ respectively of the devided stem $b_4$ and the steel capillary $g_1$ (see Comm. N⁰. 69 Pl. II) were determined in the same way as in Comm. N⁰. 78 § 13. In series I three thermometers were placed along the steel capillary, and one at the part of the glass capillary $f_2$ that remained outside the cryostat. The refrigerating action of the cryostat proving to be very slight even in the immediate neighbourhood, only three thermometers were used in the following two series, two at the ends and one in the middle of the steel capillary. The influence of an error of 1° C. in the temperature of the capillary (comp. Comm. N⁰. 78 § 13) is only $\frac{1}{4000}$ of the total compressed volume at 100° and $\frac{1}{10000}$ at $-200°$. For the temperature of the glass capillary we assumed here that indicated by the thermometer at the end of the steel capillary. This simplification is the more admissible as the temperature in the cryostat is lower, and hence the volumes outside it contain less gas.

The temperature of the glass capillary in the cryostat has been determined in the same way as was followed in the investigations with the hydrogen-thermometer mentioned in Comm. N⁰. 95*e*. As the arrangement of the cryostat was the same in the two cases, and the measuring-apparatus placed in it had almost the same form, there was no objection to start from the previously found data for the determination of the temperature of the capillary. (see Comm. N$^0$. 95$e$ § 4.) This method gives sufficient accuracy, as, reasoning in a similar way to that followed in the said communication, we arrive at the result, that an error of 50° in the temperature of the part of the stem that is taken into consideration still gives a negligible error in the final result, viz. less than $\frac{1}{5000}$.

---

[1]) Once the oil-trays near the couplings $g_1$ and $g_2$ rendered good services, when before the determinations of Series III gas escaped in consequence of the nut $g_2$ being imperfectly screwed on. From a determination of the normal-volume made immediately afterwards, it proved to have changed so much that the previous determinations had to be rejected.

The temperature $t_1$ of the piezometer-reservoir was determined by means of the resistance-thermometer, which (cf. Comm. N$^0$. 95$c$) had beforehand been compared with the hydrogen-thermometer.

They differ little from those at which the calibration of the resistance-thermometer took place. Hence the reductions are simple and may be effected with great accuracy.

The temperatures were not calculated directly from the resistance-formula of Comm. N$^0$. 95 § 6, but they were based on the separate readings of the hydrogen-thermometer, because the latter must also serve as points of the isotherms. From the above mentioned formula $\frac{dt}{dw}$ was determined, and by the aid of this factor the reduction was effected.

The difference of temperature for which the reduction was made amounting to less than 0.°3, this method of calculation is perfectly sufficient; only for the temperature of — 135°.71, where the difference amounts to 4°, a supplementary correction of 0°.01 was required.

In the subjoined table [1] the method of calculation has been represented for one determination of the temperature. The first colomn contains the observed resistance $W$, in the following column $W_c$ represents the resistance at which the resistance-thermometer has been compared with the hydrogen-thermometer (of comm. N$^0$. 95$c$ Table I § 6), and $T$ represents the corresponding reading of the hydrogen-thermometer. From the value $\frac{dt}{dw}$ and $W - W_c$ follows now the temperature-correction $\triangle t$ which is to be added to $T_c$ in order to give $t_1$ on the hydrogen-thermometer-scale.

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[1] The difference of the numbers in this table with those of the Dutch text is due to an improved calculation. The influence of this improvement enters also in some numbers of the last part of this communication.

TABLE IV. Temperature of the bath during observation N⁰. 7. of Series III

| $W$ | $W_c$ | $T_c$ | $\frac{dw}{dt}$ | $\triangle t$ | $t_1$ |
|---|---|---|---|---|---|
| 17.295 | 17.290 | — 212°.832 | 1.750 | + 0°.009 | — 212°.82 |

§ 7. *The Measurements.*

At the beginning and the end of every series the normal-volume was determined in the way described in Comm. N⁰. 78 § 12, only with this difference that in the series mentioned here every determination of the normal volume was supplemented with a reading in the $U$-tube $b_2$ and one of the barometer. In this way two determinations were generally made before and after every series. The values found before and after every series, differ nowhere more than $\frac{1}{2000}$.

The tables V and VI are analogous to the tables VII and VIII of Comm. N⁰. 78. In the former the results are represented referring to the determination of the normal volume for series III, the latter comprises the three series.

TABLE V. Normal volume $H_2$, Series III.

| N⁰. | Volume. | Pressure. | $p\,v_A$ | Mean. | Mean. | Difference. |
|---|---|---|---|---|---|---|
| 1 | 1955.78 | 75.546 | 1945.56 | 1945.58 | 1945.73 | — 0.17 |
| 2 | 1955.82 | 75.545 | 1945.60 | | | — 0.13 |
| 9 | 1961.39 | 75.342 | 1945.87 | 1945.87 | | + 0.14 |
| 10 | [1962.04 | 75.327 | 1946.13 [1] | | | + 0.40] |
| 11 | [1962.31 | 75.317 | 1946.14 | | | + 0.41] |

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[1] The two last determinations have been left out of account, though they show but slight deviations, because on account of variations of temperature in the room a certain cause could be assigned for the apparent rise of the normal-volume.

TABLE VI. Normal volumes $H_2$.

| Determinations. | | Before. | After. | Mean | Difference. |
|---|---|---|---|---|---|
| | N°. 1 | | | | — 0.05 |
| Series I | 2 | 544.74 | 544.82 | 544.78 | — 0.02 |
| | 10 | | | | + 0.02 |
| | 11 | | | | + 0.07 |
| | 1 | | | | — 0.60 |
| | 2 | 1945.73 | 1946.10 | | — 0.46 |
| | 3 | | | | — 0.23 |
| Series II | 11 | | | 1946.16 [1] | + 0.05 |
| | 12 | | | | — 0.18 |
| | 21 | 1946.10 | 1946.64 | | + 0.39 |
| | 22 | | | | + 0.58 |
| | 23 | | | | + 0.47 |
| Series III | | 1945.58 | 1945.87 | 1945.73 | see Table V |

As far as the pressure permitted, three points were chosen in every series on every isotherm for the determinations of the isotherms ascending with about equal differences of density, which offers advantages for the calculation of the virial coefficients (see § 12). The readings were adjusted at these points by bringing the mercury at the bottom, in the middle and at the top of the divided stem $b_4$. By way of control the two points in the middle and at the bottom of the stem were for some determinations determined once more with decreasing pressure.

For every determination we waited till both the temperature and the pressure were constant, and we could assume that the equilibrium of temperature and pressure had been established. This will be the case when the meniscus in the divided stem is moving up and down within the same narrow limits. The stability of the temperature was ensured by a good regulation, and that of the pressure was easily obtained and preserved by paying attention to the oiltrays mentioned in § 2, which immediately betrayed the slightest leakage [1].

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[1] A determination of the normal volume was made in this series both before and after, and also between the determinations at high pressure. The value given here is the mean from these three determinations.

When the above mentioned constant state had set in, some readings of the piezometer and the manometer were alternately made. If the latter agreed, we proceeded to the next point.

With regard to the regulation of the temperature the measurements took place under the same circumstances as the investigations with the hydrogen-thermometer described in Comm. N⁰. 95*e*. Besides the resistance-thermometer for regulation and determination of the temperature the thermo-element was also used here by way of control for the determination of the temperature. The indications of the resistance-thermometer, however, proving more reliable than those of the thermo-element, only those of the latter apparatus were used for the calculations. All possible care was always taken that the temperatures at which determinations were made, lay as close as possible to those which have been used for the calibration of the resistance-thermometer to render the corrections small, and the accuracy of the determination of the temperature as great as possible.

The regulation of the pressure took place according to the indication of the metal manometer *M* of Pl. I, fig. 1. If we passed but slowly from one pressure to the other the thermal process in the reservoir which attended it, was so slight, that the regulation and the measurement of the temperature did not experience any perceptible disturbance, on account of which the stability of the bath was the more ensured throughout a whole determination of an isotherm.

### § 8. *Calculation of the observations.*

The calculation is made in the same way as described in Comm. N⁰. 78 § 8.

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[1] Formerly this often required a long and sometimes fruitless search (cf. e.g. Comm. N⁰. 70 p. 8).

For the calculation of the variations of the volume of the piezometer reservoir $U_1$ at low temperatures we started from the quadratic formula for $k$ found in Comm. N⁰. 95*b* § 1, so that $k_1 = 23.43 \times 10^{-6}$ and $k_2 = 0.0272 \times 10^{-6}$. No correction for glass-expansion was required for the volume of the glass capillary $U_2$ nor for that of the steel capillary $U_3$. For the reduction of the gasvolume in the glass capillary $U_2$ to 0° we proceeded as follows: the volume was divided into 5 parts $U_{2a}$, $U_{2b}$, $U_{2c}$, $U_{2d}$ and $U_{2e}$. $U_{2a}$ represents the part in the liquid bath increased by 2 cm of the capillary above the liquid, where the temperature may still be put equal to that of the bath. $U_{2b}$ $U_{2c}$ and $U_{2d}$ form together the remaining part of the capillary in the cryostat above the bath, $U_{2b} + U_{2c}$ corresponds to the volume $u'_2$ of § 5 of Comm. N⁰. 95*e* and $U_{2d}$ to $u''_2$. $U_{2e}$ is the volume of the capillary that is outside the cryostat. For the reduction of the volumes $U_{2b}$, $U_{2c}$ and $U_{2d}$ we started from the same determinations of the temperature as in Comm. N⁰. 95*e*. As on account of the greater density at lower temperatures the mean temperature found cannot directly be used for the reduction, each of the above mentioned volumes is divided into 3 parts, the temperature of each of these parts is derived, and from this the mean temperature is determined according to the formula

$$t = \frac{\Sigma \frac{t}{T}}{\Sigma \frac{1}{T}}$$

in which $T$ represents the absolute temperature. The coefficients of expansion, which are required for the reduction, were determined by means of the general development into series of Comm. N⁰. 71 with a slight modification of the coefficients mentioned there. The results obtained in this way do not give an appreciable difference with those which were found when the reductions are made with the approximate results for the determinations of the isotherms obtained in this way.

With regard to the corrections of the temperature of the volumes $U_3$ and $U_4$ we proceeded in a way similar to that of Comm. N⁰. 78. For that of the reservoir at low temperature a somewhat different way was followed. As practically the temperature for every individual determination of the temperature might be considered as constant (see § 1). a number of parts of isotherms could be immediately obtained for every series separately. As they at the same time refer to about the same densities, an accurate value may be derived for $\left[\frac{d\,(pv_A)}{dt}\right]_{t_1 v_A}$ from the graphical representation of $pv_A$ on $\frac{1}{v_A}$. The temperatures in the different series not differing more than 0°.2, the results could be reduced to one and the same standard-temperature in this way without the slightest difficulty. As standard-temperatures were assumed the temperatures — 103°.57 and — 135°.71 of series I, — 182°.81 and — 195°.27 of series II, and — 204°.70, — 212°.82 and 217°.41 of series III. In the subjoined table the values of $\left[\frac{(pv_A)_{t''} - (pv_A)_{t'}}{t''-t'}\right]_{v_A} = \left[\frac{\overline{dp\,v_A}}{dt}\right]_{t'}^{t}$ [1]) are given, which served for the reduction of the remaining determinations of the isotherms to these standard temperatures $t_s$, which relate to the hydrogen-thermometer at constant volume and 1090 mM. pressure at 0°.

TABLE VII. $H_2$. $\left(\frac{\overline{dp\,v_A}}{dt}\right)_{t_{s_1}}^{t_{s_2}}$. Series II

| Density. | $\left(\frac{\overline{dp\,v_A}}{dt}\right)_{-182°.81}^{-195°.27}$ | $\left(\frac{\overline{dp\,v_A}}{dt}\right)_{-195°.27}^{-204°.83}$ | $\left(\frac{\overline{dp\,v_A}}{dt}\right)_{-204°.83}^{-212°.98}$ |
|---|---|---|---|
| 150 | 0.004336 | 0.004406 | 0.004501 |
| 160 | 0.004390 | 0.004458 | 0.004540 |
| 170 | 0.004440 | 0.004513 | 0.004588 |
| 184 | 0.004508 | 0.004599 | 0.004667 |

From these mean coefficients values for $\left[\frac{d\,(pv_A)}{dt}\right]_{t_1 v_A}$ could be derived for the different points of the respective isotherms, which for the isotherm of — 212°.82 have been given in Table XI of § 10.

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[1]) The calculation of this correction has been made simpler than in Comm. N°. 78 by introducing $\left(\frac{\overline{dp\,v_A}}{dt}\right)_1$ instead of $\alpha_{v_1}$.

### § 9. *Survey of a determination.*

As an instance of determinations of isotherms at low temperatures we give here one of the measurements from the 3rd series at a density 326 times the normal one, in oxygen boiling under strongly reduced pressure.

TABLE VIII. $H_2$ Series III N°. 7. Determination in oxygen at about — 213° C.

| Time 3.10—3.20 | A | B | C | D | E | F | G | H | K |
|---|---|---|---|---|---|---|---|---|---|
| Piezometer top | 5.8 | 56.496 | — 213° | 20°.76 | 19°.5 | | | | |
| rim | 4.8 | 56.360 | — 188° | | 19°.4 | 21.6 | | | |
| division n° 29 | 7.0 | 56.864 | — 98° | | 19°.4 | | | | |
| | | | — 11° | | | | | | |
| Manometer | | | | | | 5.0 | 93.97 | 19.98 | |
| | | | | | | | | 20.04 | |
| Piezometer top | 5.9 | 56.493 | | 20°.76 | 19°.4 | | | | |
| rim | 4.8 | 56.360 | | | | 21.6 | | | |
| | | | | | 19°.3 | | | | |
| Manometer | | | | | | 5.0 | 93.97 | 20.00 | |
| | | | | | | | | 20.05 | |
| Float | | | | | | | | | 1.3 |

The columns of the table agree in the main with those of table IX of Comm. N°. 78*b*. *A* and *B* have the same meaning, C denotes the temperature $t_1$ of the piezometer-reservoir in the bath, and the temperatures $t_{2b}$, $t_{2c}$, and $t_{2d}$ in the order of the parts $U_{2b}$, $U_{2c}$, and $U_{2d}$ (see § 8) of the glass stem in the cryostat above the bath. The temperatures given in this column are to be considered as constant throughout the determination, and have therefore been mentioned only once. *D* gives the temperature $t_4$ of the waterbath round the stem $b_4$, *E* the temperatures $t'_3$,

$t_3''$, and $t_3'''$ of the thermometers placed along the steel capillary. The temperature of the part $U_{2e}$ that projects above the cryostat is put equal to $t'_3$. The columns $F$, $G$ and $H$ have the same meaning as in the above mentioned table. In column $K$ the indication of the float in the cryostat has been given. All lengths are in cms.

These readings are corrected in the same way as was followed for table X of Comm. N$^0$. 78*b*. These corrected values are given in the following table. The two readings of the piezometer have afterwards been united to a mean after reduction.

TABLE IX. $H_2$, Series III. Determination at about — 213° C.
Corrected and adjusted data.

| | A | B | C | D | E | F | G | H | K |
|---|---|---|---|---|---|---|---|---|---|
| Manometer mean | | | | | | 115.5 | 93.97 | 19.96 | |
| Temperatures $t_1$, $t_4$, $t_3$ | | | —213° | 20°.70 | 18°.6 | | | | |
| $t_{2b}$ | | | —188° | | | | | | |
| $t_{2c}$ | | | — 98° | | | | | | |
| $t_{2d}$ | | | — 11° | | | | | | |
| Piezometer | 28.634 | 0.135 | | | | 82.3 | | | |
| | 28.631 | 0.132 | | | | | | | |
| Level of the liquid | | | | | | | | | 1.9 |

The columns from $A$ to $H$ included, have the same meaning as those of table X of Comm. N$^0$. 78*b*. $K$ denotes the position of the liquid level above the boundary of the piezometer-reservoir and the glass stem, derived from the indications of the float.

From this the following table is obtained, which gives the corrections of volume and pressure required for the calculation of $pv_A$. It corresponds to table XI of Comm. N$^0$. 78.

The volumes of the parts of the glass capillary with their corrections have been separately given. Moreover the corrections

$u'_3$ and $h$ have been added, the former is a consequence of the packings being pressed down at $g_1$ and $g_2$, the latter accounts for the weight of the compressed air in the connecting tube between the manometer and the piezometer. The vertical distance of the levels of the mercury is about 0.5 meters Instead of the mean coefficient of expansion $k$, the binomium $k_1 + k_2 t$ has been assumed (cf. § 8) for the computation of the correction $w_1$.

Here we must point out that as standard temperature $t_\alpha$ for the reduction of the parts into which the glass capillary is divided, + 20° has been assumed, so that the differences $t_\alpha - t_2$ are not very small here. The method of interpolation applied in Comm. N°. 78 for small values of $t_\alpha - t_2$ will be used as soon as we have tables for the density $d_{\alpha p_2}$ at our disposal. The values have been directly determined here by calculation.

TABLE X, $H_2$. Series III. Corrections and final result.

| | | | | | |
|---|---|---|---|---|---|
| $U_4$ = | 4.4904 | cm³ | $pm$ = | 61.004 | atm. |
| $w_4$ = | 0.0003 | » | $H_p$ = | 0.434 | » |
| $w'_4$ = | 0.0014 | » | $h$ = | − 0.004 | » |
| $u_4$ = | − 0.0104 | » | | | |
| $u_3$ = | 0.0018 | » | $u'_3$ = | − 0.0005 | cm³. |
| $U2a$ = | 0.0018 | » | $u2a$ = | 0.0059 | „ |
| $U2b$ = | 0.0020 | » | $u2b$ = | 0,0049 | » |
| $U2c$ = | 0.0025 | » | $u2c$ = | 0.0024 | » |
| $U2d$ = | 0.0129 | » | $u2d$ = | 0.0015 | » |
| $U2e$ = | 0.0190 | » | $u2e$ = | 0.0001 | » |
| $w_1$ = | − 0.0239 | » | $w'_1$ = | 0.0012 | » |
| $(pvA)t_1$ = | 0.18863 | | $t_1$ = | − 212°.82 | |
| $(pvA)_{-212°.82}$ = | 0.18863 | | for $p$ = | 61.434 | atms. |

The total value of the correction of the stem appears to be very small, so that we might apply the law of GAY-LUSSAC down to — 217° without introducing appreciable errors.

### § 10. *Values of* $pv_A$.

The values of $pv_A$ obtained in this way for the different determinations have been represented for the isotherm of — 212°.82 in the following table. The values in the last column refer to the reduction to the standard-temperature $t_s$ (cf. the conclusion of § 8).

The values of this table have been obtained, as appears from table IX, by calculation with the mean values of the separate readings. The deviations in these separate readings which may be due both to oscillations of the pressure and the temperature and to errors in the readings themselves, amount nowhere to more than $\frac{1}{2000}$.

The results found for about the same point at the beginning and at the end of one determination of an isotherm are in very good accordance, as moreover is to be seen by comparing observation N$^0$. 17 and N$^0$. 20 of table XI. The results are reduced to the same standard-temperature by means of the values of $\left[\frac{d\,(pv_A)}{dt}\right]_{t_1\,v_A}$ given in the last column.

TABLE XI. $H_2$. Results for the isotherm of — 212°.82.

| N$^0$. | | $t_1$ | $p$ | $pv_A$ | $d_A$ | $\left[\frac{d\,(pv_A)}{dt}\right]_{t_1\,v_A}$ |
|---|---|---|---|---|---|---|
| Series II | 17 | — 212°.98 | 30.591 | 0.19406 | 157.64 | 0.00458 |
| | 18 | | 35.426 | 0.19134 | 185.15 | 0.00473 |
| | 19 | | 33.071 | 0.19264 | 171.68 | 0.00465 |
| | 20 | | 30.554 | 0.19405 | 157.46 | 0.00458 |
| Series III | 6 | — 212°.82 | 51.632 | 0.18767 | 275.12 | |
| | 7 | | 61.434 | 0.18863 | 325.68 | |

TABLE XII, $H_2$ Values for $(pv_A)_{t_s}$

| N°. | | $t_s$ | $p$ | $pv_A$ | $d_A$ |
|---|---|---|---|---|---|
| $H_2$ therm. | (1) | — 103°.57 | 0.896 | 0.62082 | 1.444 |
| Series I | (2) | | 32.985 | 0.63467 | 51.971 |
| | (3) | | 39.659 | 0.63765 | 62.193 |
| | (4) | | 49.897 | 0.64274 | 77.632 |
| $H_2$ therm. | (1) | — 135°.71 | 0.727 | 0.50307 | 1.445 |
| Series I | (2) | | 28.592 | 0.51064 | 55.991 |
| | (3) | | 33.437 | 0.51258 | 65.231 |
| $H_2$ therm. | (1) | — 182°.81 | 0.479 | 0.33051 | 1.448 |
| Series II | (2) | | 46.603 | 0.32722 | 142.42 |
| | (3) | | 55.331 | 0.32845 | 168.46 |
| $H_2$ therm. | (1) | — 195°.27 | 0.413 | 0.28486 | 1.449 |
| Series II | (2) | | 40.599 | 0.27367 | 148.35 |
| | (3) | | 45.484 | 0.27337 | 166.36 |
| | (4) | | 49.998 | 0.27343 | 182.85 |
| $H_2$ therm. | (1) | — 204°.70 | 0.363 | 0.25031 | 1.449 |
| Series II | (2) | | 35.487 | 0.23189 | 153.03 |
| | (3) | | 38.640 | 0.23097 | 167.30 |
| | (4) | | 42.438 | 0.23010 | 184.43 |
| Series III | (5) | | 61.917 | 0.23009 | 269.10 |
| $H_2$ therm. | (1) | — 212°.82 | 0.320 | 0.22056 | 1.450 |
| Series II | (2) | | 30.689 | 0.19480 | 157.64 |
| | (3) | | 33.200 | 0.19339 | 171.68 |
| | (4) | | 35.566 | 0.19210 | 185.15 |
| Series III | (5) | | 51.632 | 0.18767 | 275.12 |
| | (6) | | 61.434 | 0.18863 | 325.68 |
| $H_2$ therm. | (1) | — 217°.41 | 0.295 | 0.20375 | 1.450 |
| Series III | (2) | | 46.419 | 0.16381 | 283.81 |
| | (3) | | 52.898 | 0.16336 | 323.80 |
| | (4) | | 58.971 | 0.16422 | 359.04 |

In table XII the results obtained in this way are also given for the remaining isotherms. Those belonging to series I are less certain and will be repeated.

The results obtained at the beginning and at the end of a determination of an isotherm at about the same density have been united to a mean.

For every temperature we have added to the results of the determinations of isotherms those of the readings of the hydrogen-thermometer to which the former are in direct relation.

The Nos do not agree with those of the preceding table, because some determinations have been united to a mean, for which reason they are indicated by ( ).

The points of the hydrogen-thermometer have been obtained in the following way. From SCHALKWIJK's determinations of isotherms follows for 20° C.

$$pv_A = 1.07258 + 0.000667\, d_A + 0.00000099\, d_A^2.$$

If we suppose the mean pressure-coefficient from 0° to 20° not to deviate appreciably from the value 0.0036627 between 0° and 100°, which is permissible on account of the insignificant deviations of the indications of the hydrogen-thermometer of constant volume from the absolute scale, it follows from this that:

$$(pv_A)_{0^\circ,\ 1100\ mm.} = 1.000275.$$

The value given in Comm. N$^0$. 60 having been taken for the pressure-coefficient of hydrogen for the calculation of the hydrogen thermometer-temperatures, the value of $pv_A$ at $t_s$ now follows from the formula

$$(pv_A)_{t_s} = (pv_A)_0\ (1 + 0.0036627\ t_s).$$

§ 11. *Probable error of a determination.*

The mean error in the calibration of the large volume of the piezometer may be estimated at $\pm \frac{1}{4000}$. As to the volume into which the gas is compressed during the measurements, the greater density of the gas in the reservoir at low temperatures may be allowed for by reckoning only with $\frac{1}{3}$ of the amount of the volumes at the temperature of the room. The errors in these volumes being predominant with respect to those in the volume of the piezometer-reservoir, the mean error for measurements below — 180° with piezometers of 5 c.M$^3$ may be put equal to $\pm \frac{1}{3000}$ of the compressed volume in accordance with the degree of accuracy as was calculated in Comm. N$^0$. 69, where for measurements at the ordinary temperature the mean error is estimated at $\pm \frac{1}{1000}$ for piezometers of 5 c M$^3$. For — 100° the mean error will be $\pm \frac{1}{2000}$.

The mean error of the determinations of the normal volume is $\pm \frac{1}{3000}$, that of the measurements of the pressure may also be estimated at $\pm \frac{1}{3000}$.

In the determination of the temperature there is no appreciable error. The observations made for one point show that the mean error due to variations of temperature and to accidental errors in reading the position of the mercury in the stem, may be put smaller than $\pm \frac{1}{5000}$.

The mean error of the determination of temperature in the stem remains below $\pm \frac{1}{6000}$.

The mean error caused by all these sources of errors together amounts to $\pm \frac{1}{1500}$ for piezometers of 5 c M.$^3$ and not very low temperature, to $\pm \frac{1}{1700}$ for larger piezometers and very low temperature. The different points on one and the same isotherm must show smaller discrepancies inter se than corresponds with the said mean error. The mean error namely, for a determination, apart from the errors in the determination of the normal volume and the calibration of the large volume is

$$\text{from } \pm \frac{1}{2000} \text{ to } \pm \frac{1}{2400}.$$

## § 12. *Provisional individual virial coefficients.*

If the temperatures had not been given as readings on the hydrogen-thermometer of constant volume at 1100 mm. pressure, but on the absolute scale, the coefficients $A_A$, $B_A$ etc. calculated from the equation

$$pv_A = A_A + \frac{B_A}{v_A} + \frac{C_A}{v^2_A} + \frac{D_A}{v^4_A} + \frac{E_A}{v^6_A} + \frac{F_A}{v^8_A} \quad \ldots . \quad (1)$$

with the values of $pv_A$ from table XII, could be immediately compared with those derived in Comm. N⁰. 71 [1]. However, this is not the case, because the latter relate to the absolute scale of temperature. From the outset it has been our purpose to derive the correction of the hydrogen scale to the absolute scale experimentally from our measurements themselves. This might be attained by first neglecting the correction, and by calculating provisional values $A'_A$, $B'_A$, $C'_A$ etc. for each of the isotherms, which serve then for finding provisional corrections for the hydrogen-thermometer; after this the calculation is repeated with the corrected temperatures, etc., till further repetition would not bring about any change. A similar treatment has been applied for the determination of the corrections of the readings of the hydrogen-thermometer to the absolute scale, where we purposed to draw through the observations for every isotherm a curve, which does not only correspond as closely as possible to the observations, but also to the general equation of state. In this § the method of least squares has been applied directly to the individual isotherms, in order to obtain a formula which represents the observations as accurately as possible.

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[1] We must call attention to the fact that in the calculations of Comm. N⁰. 71 we began by taking 273°.04 as a first approximation for the absolute zero-point; we should find the correction to this from the results of the calculations of isotherms, and then proceed to a second approximation. We have still retained 273°.04 in the coefficients VI. 1 (Suppl. N⁰. 8) and in VI. 2 (Comm. N⁰. 92). Since then, however, a set of coefficients VII. 1, which will be published in a following communication, have been calculated with the further approximation for the absolute temperature, viz. the more accurate value 273°.09, and corrections have, moreover, been applied to critical quantities etc.

The number of points on each isotherm not being large enough for all six coefficients to be determined at once, definite values were assumed for the last three values. $F_A$ was put $= 0$, and values were calculated for $D_A$ and $E_A$ from the sets of coefficients VII. 1 [1], which was chosen instead of V of Comm. N°. 71. This assumption means, that a definite course was prescribed for the isotherms at higher densities, which corresponds as closely as possible to the law of the corresponding states. The results of these calculations are laid down in the subjoined table. $D_A$ and $E_A$ are the values assumed for the calculation according to the above.

TABLE XIII. $H_2$. Provisional virial coefficients.

| $t_S$ | $A'_A$ | $10^3.B'_A$ | $10^6.C'_A$ | $10^{12}\,D'_A$ | $10^{18}.E'_A$ |
|---|---|---|---|---|---|
| — 103°.57 | 0.62048 | 0.24271 | 0.5584 | 0.9113 | — 0.648 |
| — 135°.71 | [0.50303 | 0.03234 | 1.7974 | 0.7028 | — 0.408] |
| — 182°.81 | 0.33063 | — 0.08384 | 0.4021 | 0.3809 | — 0.088 |
| — 195°.27 | 0.28503 | — 0.13051 | 0.3565 | 0.2892 | — 0.016 |
| — 204°.70 | 0.25058 | — 0.18030 | 0.3710 | 0.2166 | 0.031 |
| — 212°.82 | 0.22090 | — 0.22433 | 0.3668 | 0.1514 | 0.066 |
| — 217°.41 | 0.20410 | — 0.25013 | 0.3715 | 0.1122 | 0.082 |

It appears from the table, that the coefficients of the same column vary regularly with the temperature, except for — 135°.71, for which we may account by taking into consideration that the two piezometer-determinations which had to be used for the calculation, lie so close together, that a slight difference in their relative situation already produces a large difference in $B'_A$ and $C'_A$.

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[1] For the calculation of $D_A$ and $E_A$ the uncorrected reading of the hydrogen thermometer was used (see preceding note).

By the aid of the coefficients the values of $pv_A$ were determined anew according to formula (1). The divergencies for every isotherm between the assumed values of $pv_A$, $O_i$ and the $C_{0i}$ calculated with $A'_A$, $B'_A$ and $C'_A$ ($pv_A = 1$ for 0° and 760 mm.), where $i$ indicates the number of that observation in table XII, have been represented in the subjoined table.

TABLE XIV $H_2$. Deviations from formula (1).

| | $10^5 (O_i - C_{oi})$ | | | | | | in % of $C_{oi}$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $t_S$ | $i=1$ | $i=2$ | $i=3$ | $i=4$ | $i=5$ | $i=6$ | $i=1$ | $i=2$ | $i=3$ | $i=4$ | $i=5$ | $i=6$ |
| —103°.57 | — 1 | + 7 | — 9 | + 3 | | | 0.001 | 0.011 | 0.015 | 0.005 | | |
| —135°.71 | | | | | | | | | | | | |
| —182°.81 | | | | | | | | | | | | |
| —195°.27 | + 1 | + 1 | — 4 | + 2 | | | 0.004 | 0.004 | 0.014 | 0.007 | | |
| —204°.70 | — 1 | + 9 | 0 | - 9 | + 1 | | 0.004 | 0.036 | 0.000 | 0.036 | 0.004 | |
| — 212°.82 | — 2 | + 5 | + 6 | - 2 | — 17 | + 10 | 0.007 | 0.022 | 0.027 | 0.009 | 0.077 | 0.045 |
| —217°.41 | 0 | 0 | — 3 | + 2 | | | 0.001 | 0.000 | 0.014 | 0.010 | | |

The isotherm of — 212°.82 is best adapted to give an idea of the accuracy of the mutual agreement on account of its larger number of points. The agreement proves very satisfactory. The upper limit of the mean error may be put at $\pm \frac{1}{2000}$.

§ 13. *Minima of pv.*

By means of the coefficients of table XIII the minima of the *pv*-curves given in table XV were derived from the data of table XII.

By means of the method of least squares the coefficients of a parabola

$$p = P_0 + P_1 (pv_A) + P_2 (pv_A)^2$$

TABLE XV. $H_2$ Minima of $p v_A$.

| $t_S$ | $pv_A$ | $d_A$ | $p$ | $O - C_0$ |
|---|---|---|---|---|
| — 182°.81 | 0 32630 | 102.24 | 33.36 | — 0.08 |
| — 195°.27 | 0.27338 | 174.45 | 47.69 | + 0.50 |
| — 204°.70 | 0.22935 | 227.17 | 52.10 | — 0.75 |
| — 212°.82 | 0.18780 | 285.55 | 53.63 | + 0.26 |
| — 217°.41 | 0.16335 | 315.72 | 51.57 | + 0.08 |

have been calculated from these data. They are:

$$P_0 = - 2.623$$
$$P_1 = 552.610$$
$$P_2 = - 1354.86$$

The differences $O - C_0$ between the given values of $p$ and those calculated with these coefficients have been represented in the last column of table XV. They amount to little more than $^1/_2$ atmosphere. The results given in the table have been reproduced in a diagram on Pl. II [1]; the curve traced there is the calculated parabola.

It follows further from the values of the coefficients, that the parabola cuts the ordinate $p = 0$ in two points, where $pv_A$ is respectively 0.00480 and 0.40307, from which follows with the formula [2])

$$(pv_A)_T = 0.99939 \; [\, 1 + 0.0036618 \, (T - 273°09) \,]$$

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[1]) The temperatures have been given in absolute degrees below zero. The temperatures noted down on the plate undergo slight alterations on account of a more accurate calculation of the corrections to the absolute scale. They become — 103°.54, — 135°.67, — 182°.75, — 195°.20, — 204°.62. — 212°.73 and — 217°.32.

[2]) This value of $A_{A0}$ has been calculated from SCHALKWIJK's determinations of isotherms (cf. the conclusion of § 10).

for the corresponding temperatures measured on the absolute scale,

$$T_1 = 1^\circ.3 \qquad\qquad T_2 = 110^\circ.2.$$

The top of the parabola lies at a pressure of 53.73 atms.; the value of $pv_A$ is here 0.20394, from which follows, in connection with the value of $\left(\frac{d\,(pv_A)}{dt}\right)_{p\,=\,53.73}$ determined from the isotherms, viz. 0.0053, for the absolute temperature of the isotherm which passes through the top that

$$T = 63^\circ.5$$ [1].

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[1] In this the corrections to the absolute scale have been taken into account.

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

## No. 97$^b$.

**Dr. H. KAMERLINGH ONNES and C. BRAAK.** "On the measurement of very low temperatures. XIV. Reduction of the readings of the hydrogen-thermometer of constant volume to the absolute scale." (*With a plate*).

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam* **26 Januari 1907**, p. 668—677).

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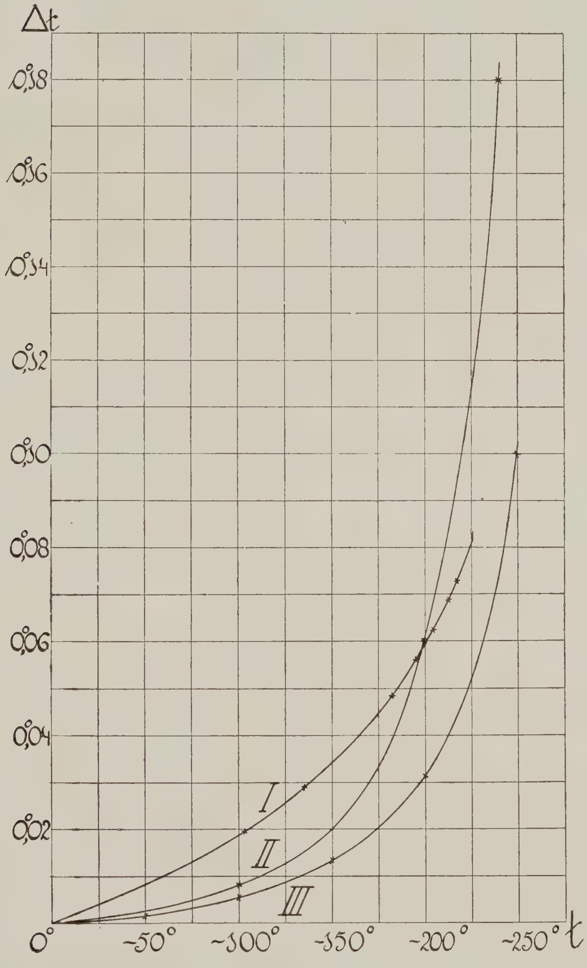

Communication No. 97$^b$.

## **Dr. H. KAMERLINGH ONNES and C. BRAAK.** „*On the measurement of very low temperatures. XIV. Reduction of the readings of the hydrogen-thermometer of constant volume to the absolute scale.*

### § 1. *Introduction.*

As it is till now difficult to obtain pure helium, and very well possible to obtain pure hydrogen (cf. Comm. N⁰. 94*f*) the scale of the normal hydrogen-thermometer (that with constant volume and a pressure of 1000 m.M. of mercury at 0°) is for the present, just as when it was first mentioned (1896) as the basis of the measurement of low temperatures at Leiden in the first communication (N⁰. 27) on this subject, still the most suitable temperature-scale to indicate low temperatures down to — 259° unequivocally with numerical values, which come nearer to the absolute scale than those on any other scale. It is therefore of great importance to know the corrections with which we pass from the normal hydrogen-scale to the absolute one.

As is known they may be calculated for a certain range of temperatures, when the equation of state for this range of temperatures has been determined at about normal density. Up to now we had to be satisfied for that calculation for the hydrogen-thermometer below 0° with equations of state of hydrogen obtained in a theoretical way. BERTHELOT [1]) derives them by means of the law of corresponding states from experimentally determined data of other substances in the same region of reduced temperature. CALLENDAR [2]) modified VAN DER WAALS' equation of state so as to render it adapted to represent the results of the experiments of JOULE-KELVIN for air and nitrogen as well as those for hydrogen between 0° and 100°, and supposes that a same form of equation holds also for hydrogen outside this region. Upon the main this comes to the same thing as the application of the law of corresponding states, albeit to a limited group of substances. Though such theoretical corrections as have been given by BERTHELOT and CALLENDAR are a welcome expedient to help us in default of other data [1]) yet an experimental determination of these corrections remains necessary.

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[1]) Sur les thermomètres à gaz, Travaux et Mémoires du Bureau International, T. XIII.

[2]) Phil. Mag. [6] 5, 1903.

We have obtained them in this research by using the isotherms of hydrogen between — 104° C. and — 217° C. given in Comm. N⁰. 97*a*.

For the calculation of these corrections at a definite temperature we might start from the individual virial coefficients in the development into series of the equation of state (cf. Comm. N⁰. 71), which we have derived in § 12 of Communication N⁰. 97*a*. The results obtained in this way show really a regular course [2]), in spite of the small number of points on the isotherms.

However, we wished first to adjust the results of the separate isotherms by general formulae of temperature. Both in this case and in general it is very difficult to succeed in this by application of one of the equations of state drawn up in a finite form. Very suitable for such a purpose is the general development into series (or more strictly speaking, development into a polynomial) which has already been mentioned frequently. We chose for this the

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[1]) WROBLEWSKI's determinations of isotherms at the boiling point of ethylene and oxygen are not accurate enough for this purpose. In the results found for the last temperature this is immediately apparent from the irregular situation of the points on the isotherm. The values obtained at the boiling-point of ethylene give more harmonious results. And yet a correction on the absolute scale would follow from them which has the wrong sign, viz. — 0°.07.

At the temperature of liquid air TRAVERS has determined the difference between the hydrogen-thermometer of constant volume and that of constant pressure, from which we may also derive the corrections to the absolute scale for these temperatures. It is obvious that this derivation cannot be very trustworthy.

Further it is now possible (see § 1 of Comm. N⁰. 97*a*) to derive data on the expansion of hydrogen at low temperatures from the determinations of WITKOWSKI; they will be discussed in a following communication.

[2]) Only the isotherm of — 135°.71 gives a deviating result. (See the conclusion of § 12 of the preceding communication.)

For insertion in Vol. IX, Nos. **97–108**.

## Errata Communication N⁰. 97.

p. 33 at the bottom after formula (2) read a footnote: „1) $B'_T$ and $C'_T$ have to be well distinguished from the provisional virial coefficients $B'_A$ and $C'_A$ in Table XIII Comm. N⁰. 97*a*".

p. 34 note 1 line 2 from the bottom: omit: „(see XV)".

p. 35 line 9 from the top: for „(see XV at the end of this Communication)" read: „(comp. Comm. N⁰. 102*d*)".

p. 36 line 6 from the top: for „(2)" read: „(3)".

p. 36 note 2 line 2 from the bottom: for „proceding" read „preceding".

form VII. 1 (cf. the footnote to § 12 of Comm. N$^0$. 97*a*). The adjustment takes place by calculating for every isotherm modifications in $B$ and $C$, $\triangle B$ and $\triangle C$, which we call individual $\triangle B$ and $\triangle C$, with an approximate value of the correction to the absolute scale, by then representing the values of $\triangle C$ by a general formula of the temperature, and by computing new values for $\triangle B$ by successive approximation in such a way that the value for the correction on the absolute scale corresponds to the assumed value of $T$. Finally also the values of $\triangle B$ were represented by a general formula of the temperature.

If we put the new values of $B$ and $C$ obtained by the aid of these corrections, which *special* values we denote by VII. $H_2$. 1, in the polynomial of state, then this represents at the same time the determinations of isotherms of Comm. N$^0$. 70 at 20° very satisfactorily, and those of Comm. N$^0$. 78 at 0° and 20° by approximation.

By means of these general expressions the reductions on the absolute scale have been carried out.

If $B$ and $C$ are known there is another way to derive the absolute temperature from the observations with the hydrogen thermometer, than by applying the corrections which lead from the hydrogen scale to the absolute temperature scale In the calculation of the temperature from the observations we may namely take at once into account, that the gas in the thermometer does not follow the law of BOYLE-CHARLES, but that pressure and volume are connected in the way, as is indicated by the development into series with the corrected values of $B$ and $C$. The formula which may serve for this purpose, is given in § 5.

### § 2. *Reduction of the readings of the hydrogen-thermometer of constant volume to the absolute scale.*

If $v$ is the volume of the gas in the thermometer, expressed in the theoretical normal volume, $p$ the pressure in atmospheres, $T$ the absolute temperature, the equation of state for the thermometer-gas may be written in the form :

$$pv = A_T\left(1 + \frac{B'_T}{v} + \frac{C'_T}{v^2}\right) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Further we put:

$t$ the temperature on the scale of the hydrogen-thermometer of constant volume

and $$T - T_{0^\circ \mathrm{C.}} = \theta.$$

$t$ is determined by

$$t = \frac{(p\,v)_T - (p\,v)_0}{(p\,v)_0\ \alpha_v},$$

where $\alpha_v$ represents the mean pressure-coefficient between 0° and 100° for the thermometer with the specific volume $v$. This is given by $\dfrac{(p\,v)_{100} - (p\,v)_0}{100\,(p\,v)_0}$.

If we represent the correction on the absolute scale by:

$$\triangle t = \theta - t,$$

we may write for this:

$$\triangle t = \frac{(T - T_0)\left(\dfrac{T_{100}\,B'_{100} - T_0 B'_0}{100\,v} + \dfrac{T_{100}\,C'_{100} - T_0\,C'_0}{100\,v^2}\right)\quad\left(\dfrac{TB'_T - T_0 B'_0}{v} + \dfrac{T\,C'_T - T_0\,C'_0}{v^2}\right)}{1 + \dfrac{T_{100}\,B'_{100} - T_0 B'_0}{100\,v} + \dfrac{T_{100}\,C'_{100} - T_0 C'_0}{100\,v^2}} \tag{3}$$

In agreement with what may be derived from the mean equation of state VII. 1, it appears from our determinations, that the influence of $C'_T$ is very slight, and down to — 217° does not amount to more than 0°.0003, so that it has not to be taken into account. Therefore in what follows will be put $C'_T = 0$, as is also done by BERTHELOT but without proof.

For the absolute zero-point the value 273°.09 [1]) is assumed, from which follows $A_T = 0.0036618\ T$, $T_{0°C} = 273°.09$ and $T_{100°\,C.} = 373°.09$.

---

[1]) From AMAGAT's experiments with the development into series of Comm. N°. 71 (cf. the note to § 12 of Comm. N°. 97*a*) $1.26 \times 10^{-5}$ was found for the difference between the pressure-coefficients of nitrogen at 1000 mm. pressure and 0 mm. pressure, from which follows with CHAPPUIS' pressure-coefficient for 1000 mM., i. e. 0.0036744 the value 0.0036618 for the limiting value at 0 mM. pressure, corresponding to the absolute zero-point — 273°09. In the same way hydrogen gives for the difference of the pressure-coefficients at 1090 m.M. and 0 m.M. $2.1 \times 10^{-6}$, which with the pressure-coefficient 0.0036629 given in Comm. N°. 60 (see XV) gives the limiting value 0.0036608. The same value as was found above from nitrogen, was derived by BERTHELOT (loc. cit.)

For the reduction of the data given in Comm. N⁰. 97*a* to the theoretical normal volume the value $\frac{v_A}{v} = 0.99939$ was taken, borrowed from the determinations of isotherms of Comm. N⁰. 70 (SCHALKWIJK).

The values of $B'_0$ and $B'_{100}$ have been derived from the same determinations of isotherms [1]) by the aid of the pressure-coefficient 0.0036629 (see XV at the end of this Communication) neglecting the correction to the absolute scale for 20°. These values are : [2])

$$B'_0 = 0.000607 \qquad B'_{100} = 0.000664.$$

The values of $B'_T$ were found from the VII. $H_2$. 1 already more fully discussed in § 1, which gives in the reduced form [3])

$$10^8\,\mathfrak{B} = +173.247\,t - 462.956 - 706.416\frac{1}{t} + 384.2458\frac{1}{t^3} - 4.2530\frac{1}{t^5}$$

whereas VII. 1 gives :

$$10^8\,\mathfrak{B} = 157.9500\,t - 305.7713 - 231.8247\frac{1}{t} - 97.5686\frac{1}{t^3} - 4.2530\frac{1}{t^5}$$

From this the values of $B'_T$ have been calculated for the standard-temperatures of the isotherms.

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from CHAPPUIS' results for nitrogen and those for hydrogen obtained with a thermometer-reservoir of hard glass. In the same paper he derives the value 273°.08 for the absolute zero-point for the case that also the less concordant results found by CHAPPUIS for hydrogen with a platinum-thermometer are taken into account. Afterwards (see Zeitschrift für Elektrochemie N⁰. 34, 1904) the first mentioned value 273°.09 is again found by taking the mean of the above values for nitrogen and hydrogen, and those which may be derived by means of the experiments of KELVIN and JOULE.

[1]) Compare the conclusion of § 10 of Comm. N⁰. 97*a*.

[2]) The values found by CHAPPUIS are resp 0.000579 and 0.000606.
Those of WITKOWSKI are 0.000616 and 0.000688.
Those derived in Comm. N⁰. 71 from the observations of AMAGAT are 0.000669 and 0.000774.

[3]) According to DEWAR, $p_k = 15$ atms. and $T_k = 29°$ are used for the calculation, which also served for the derivation of VII. 1.

Furter have been put $A_{A_0} = 0.99939$ and $A_A = A_{A_0}\ (1 + 0.0036618\ t)$.

The subjoined table contains in the first column these standard temperatures $t_s$ measured on the scale of *our* hydrogen-thermometer [1]), in the second column the same temperatures measured on the absolute scale The two following columns contain the corresponding values of the special $B'_T$ and of the corrections to the absolute scale $\triangle t_s$ calculated according to formula (2) for a hydrogen-thermometer of constant volume with 1090 mm. zero-point-pressure. The last column gives the corrections for the *normal* hydrogen-thermometer.

The values for — 135°.70 are less certain than the others (compare § 10 and § 11 of the preceding communication).

TABLE XVI. $H_2$ Corrections to the absolute scale.

| $t_s$ | $\theta$ | $B'_T.10^3$ | $\triangle t_s$ | $\triangle t$ |
|---|---|---|---|---|
| — 103°.56 | — 103°.54 | + 0.3892 | 0°.0214 | 0°.0196 |
| — 135°.70 | — 135°.67 | + 0.2368 | 0°.0316 | 0°.0290 |
| — 182°.80 | — 182°.75 | — 0 2327 | 0°.0530 | 0°.0486 |
| — 195°.26 | — 195°.20 | — 0.4734 | 0°.0611 | 0°.0561 |
| — 204°.69 | — 204°.62 | — 0.7244 | 0°.0683 | 0°.0627 |
| — 212°.81 [2]) | — 212°.73 | — 1.0112 | 0°.0752 | 0°.0690 |
| — 217°.40 | — 217°.32 | — 1.2467 | 0°.0796 | 0°.0730 |

With very close approximation the result of the last column may be represented by the formula:

$$\triangle t = a\frac{t}{100} + b\left(\frac{t}{100}\right)^2 + c\left(\frac{t}{100}\right)^3 + d\left(\frac{t}{100}\right)^4 \quad . \; . \quad (4)$$

---

[1]) The slight differences with the value of table XII of Comm. N°. 97*a* are due to a correction (see XV) in consequence of the application of the improved pressure-coefficient 0.0036629 and the influence of the dead space on the determinations of the temperature, which will be more fully discussed in the last part of this communication.

[2]) The difference with Comm. N°. 97*a* remaining after the correction of the proceding note is the consequence of an improvement applied in the calculation.

where:

$$a = -\ 0.0143307$$
$$b = +\ 0.0066906$$
$$c = +\ 0.0049175$$
$$d = +\ 0.0027197$$

The greatest deviation is three units of the last decimal.

The formula gives the value $\triangle t = 0$, both for $t = +100°$ and for $t = 0°$, while $\triangle t = +0°.14$ would follow from it for $t = -273°$.

§ 3. *Accuracy of the corrections.*

The influences which may cause errors in the corrections, are of two kinds.

1. Errors in the values of $B'_T$.

2. Errors in the data which have been used in the further derivation. The latter may be reduced to the error in $B'_0$ and the difference of the pressure-coefficients used for the density $= 0$ and that at 0° and 1090 mM. If for the mean error in $B'_0$ we compare the values of $B'_0$ which may be derived from the data of Comm. N$^{os}$. 70 and 78 and from those of Chappuis, a mean error of ± 0.000034 (about agreeing with the error per cent. derived for the $pv$ in § 11 of Comm. N$^0$ 97*a*) follows from their deviations inter se, which corresponds with a mean error of ± 0°.008 at $-100°$ and of ± 0°.003 at $-200°$ for $\triangle t$.

We may further assume that the mean error in the pressure-coefficients 0.0036618 and 0.0036629 amounts to one unit of the last decimal for the first and to two units for the second, which corresponds with a mean error in $\triangle t$ of ± 0°.003 and ± 0°.006 at $-100°$ and of ± 0°.005 and ± 0°.011 at $-200°$.

If we further put the mean error in $B'_T$ equal to that of $B'_0$, a mean error in $\triangle t$ corresponds to this of ± 0°.006 at $-100°$ and of ± 0°.002 at $-200°$.

The total mean error in consequence of all these mean errors together will amount to ± 0°.012 for $-100°$ and 0°.013 for $-200°$.

§ 4. *Comparison of the results with those which have been theoretically derived.*

Table XVII contains the corrections concerning the normal hydrogen-thermometer. Besides the above mentioned values of $\triangle t$, which were directly found from the observation it contains the corrections determined according to the serial formula VII. 1 and those calculated by Callendar and Berthelot. Moreover in the last column the corrections, which may be calculated from the experimental values adjusted with VII. $H_2$ according to formula (4) are given for a comparison.

TABLE XVII. $H_2$. Corrections to the absolute scale.

| $t$ | $\Delta t$ | | $t$ | $\Delta t$ | | |
|---|---|---|---|---|---|---|
| | experimental values | according to VII. 1 | | according to CALLENDAR | according to BERTHELOT | from experimental values |
| — 103°.56 | 0°.0196 | 0°.0017 | — 10° | 0°.00021 | | 0°.0015 |
| — 134°.70 | 0°.0290 | 0°.0032 | — 20° | 0°.00048 | | 0°.0031 |
| — 182°.70 | 0°.0486 | 0°.0082 | — 50° | 0°.00164 | | 0°.0082 |
| — 195°.26 | 0°.0561 | 0°.0108 | — 100° | 0°.0054 | 0°.008 | 0°.0187 |
| — 204°.69 | 0°.0627 | 0°.0136 | — 150° | 0°.0132 | | 0°.0337 |
| — 212°.81 | 0°.0690 | 0°.0168 | — 200° | 0°.0311 | 0°.06 | 0°.0593 |
| — 217°.40 | 0°.0730 | 0°.0192 | — 240° | | 0°.18 | |
| — 240° | | 0°.0470 | — 250° | 0°.1005 | | |
| — 250° | | 0°.0470 | | | | |

Besides the corrections derived from this investigation for the zero-point-pressure of 1000 m.M., also the values found by Berthelot and Callendar are represented on the plate. The three curves have been indicated by I, II and III in the above mentioned order. Also II and III refer to a zero-point-pressure of 1000 m.M.

The values derived by CALLENDAR and BERTHELOT by means of the law of corresponding states appear to deviate systematically from the experimental ones. With regard to the corrections according to VII, 1., in the derivation of which formula agreement in the region of the equation of state (between 0° and — 217° for hydrogen) treated here, was not aimed at, we may observe that a modification is required for VII. 1 to give as good an agreement as possible also in this region. In the first place this agreement would require that for the calculation of VII. 1 those values were assumed for the critical quantities of $H_2$ which follow from the data of Comm. N$^0$. 97*a*. They are $p_k = 15$ atms. and $T_k = 43°$. This value of $T_k$ would considerably increase the corrections given in table XVII according to VII. 1.

§ 5. *Formula to derive the temperature directly from the observations with the gas-thermometer of constant volume.*

We suppose that the correction for the difference in pressure at the mercury meniscus and the thermometer-reservoir in consequence of the weight of the thermometer-gas is applied to $H_T$, and that it is so small that it may be neglected for the small volumes.

The fundamental formula for the reduction is [1]:

$$p\,v = A_T\left(1 + \frac{B_T}{v} + \frac{C_T}{v^2}\right)$$

which may also be written in the form:

$$p\,v = A_T\left(1 + B_T^{(p)}\,p + C_T^{(p)}\,p^2\right) \quad . \quad . \quad . \quad . \quad (5)$$

We start from this latter formula. The equation for the gas-thermometer (cf. formula (1) of § 5 of Comm. N$^0$. 95*e*) becomes now:

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[1] Here $v$ is expressed in the theoretical normal volume and hence $A_T = 1 + 0.0036618\,\theta$. We call the value for 0° C., at which $\theta = 0$, $A_{T_0}$. It is 1.

$$H_T \left[ \frac{V_0 (1 + k_1 t + k_2 t^2) + \beta_1 + u_1}{A_T (1 + B_T^{(p)} H_T + C_T^{(p)} H_T^2)} + \frac{u_2'}{A_{t_2'} (1 + B_{t_2'}^{(p)} H_T^2)} + \right.$$

$$\left. + \frac{u_2''}{A_{t_2''} (1 + B_{t_2''}^{(p)} H_T)} + \frac{u_3}{A_{t_3} (1 + B_{t_3}^{(p)} H_T)} + \frac{u_4}{A_{t_4} (1 + B_{t_4}^{(p)} H_T)} \right] =$$

$$= H_0 \left[ \frac{V_0 + \beta_2 + u_1 + u_2' + u_2'' + u_2'''}{A_{T_0} (1 + B_{T_0}^{(p)} H_0 + C_{T_0}^{(p)} H_0^2)} + \frac{u}{A_{15} (1 + B_{15}^{(p)} H_0)} \right] \quad (6)$$

This formula holds also for the carbonic-acid-thermometer up to the number of decimals given by Chappuis. In XV we shall further discuss the deviation from the formula used by Chappuis.

With a sufficient degree of approximation the formula for the determination of the temperature down to 0°.001 with a hydrogen thermometer of 1100 m.M. zero-point-pressure and a dead space $\frac{u}{V_0} < 0.01$ may be written in the simpler form:

$$H_T \left[ \frac{V_0 (1 + k_1 t + k_2 t^2) + \beta_1 + u_1}{A_T (1 + B_T^{(p)} H_T)} + \frac{u_2'}{1 + 0.00366\, t_2'} + \right.$$

$$\left. + \frac{u_2''}{1 + 0.00366\, t_2''} + \frac{u_3}{1 + 0.00366\, t_3} + \frac{u_4}{1 + 0.00366\, t_4} \right] =$$

$$= H_0 \left[ \frac{V_0 + \beta_2 + u_1 + u_2' + u_2'' + u_2'''}{A_{T_0} (1 + B_{T_0}^{(p)} H_0)} + \frac{u}{1 + 0.00366 \times 15} \right] \quad (7)$$

First an approximate value may be assumed for $B_T^{(p)}$. With the approximate value of the temperature found in this way a better value of $B_T^{(p)}$ may be determined, and the correction-term for the expansion of glass calculated.

Thus we find $A_T$, from which the value of $\theta$ follows though

$$\frac{A_T - A_{T_0}}{0.0036618} = \theta.$$

## XV. *Influence of the deviation from the law of* Boyle-Charles *on the temperature, measured with the scale of the gas-thermometer of constant volume according to the observations with this apparatus.*

§ 1. When the formulae are drawn for the calculation of the temperature on the scale of the gas-thermometer of constant volume the variation of pressure of the gas both in the thermometer-reservoir and in the dead space has as yet (see e. g. Chappuis) been generally entered into the calculation as if it took place at perfectly constant density.

The error committed in this way, is so slight for the permanent gases for small values of the dead space, that it manifests itself only in the last of the decimals given by Chappuis. For Chappuis' carbonic-acid-thermometer, however, it attains an appreciable value (the influence extends here to the last decimal but one), so that it was of importance to examine in how far it is permissible to neglect it. This appears when Chappuis' formula is more closely compared with formula (6) of XIV.

The density not being constant, either in the thermometer-reservoir nor in the dead space, on account of the fact that e g. at low temperatures gas passes from the dead space to the reservoir, and $pv$ as well as the pressure-coefficient varies with the density, four approximations are applied in this treatment (two for reservoir and two for dead space), all giving an error in the same direction. (Adsorption is left out of account).

The errors caused by these approximations, are of the same order of magnitude for the reservoir and the dead space, the first applying to a large volume and a small difference of density, the second to a small volume and a large difference of density. The correction which is to be applied to the determination of temperature on account of these errors, only amounts to — 0°.001 at — 100° for a hydrogen-thermometer with 1000 mm. zero-point-pressure and a dead space of 0.01 $V_0$, to somewhat less for lower temperatures, and so it may be neglected below 0°.

Formula (6) differs from the preceding formula by one correction more, which is independent of the size of the dead space, and which is the result of the variation of density in the reservoir caused by the expansion of the glass. This error is of no importance for the determination of the temperature by the hydrogen-thermometer, but may exercise an appreciable influence in some cases. (cf. § 3).

The approximations mentioned have also an influence on the determination of the mean pressure-coefficient. The discussion, perfectly analogous to that for the influence on the determination of the temperature, gives + 0.00000019 as correction for our thermometer, which remains below the limit of accuracy given in Comm. N°. 60. Hence the value 0.0036627 derived in Comm. N°. 60 for hydrogen at 1090 mm. changes into the corrected value 0.0036629.

§ 2. We may pass from the temperatures derived in the way mentioned in Comm. N°. 95*e* to those on the normal hydrogen-thermometer by availing ourselves of the subjoined table, in which the corrections required for this have been given. These corrections give an account of the variation in the assumed pressure-coefficient and (with regard to the number of decimals given) of the influence of the dead space.

TABLE XVIII. Corrections for the temperatures calculated according to Comm. N°. 95*e* to those on the normal hydrogen-scale.

| $t$ | $\Delta t$ | $t$ | $\Delta t$ |
|---|---|---|---|
| — 50° | + 0°.003 | — 200° | + 0°.016 |
| — 100° | + 0°.006 | — 220° | + 0°.019 |
| — 150° | + 0°.010 | — 250° | + 0°.020 |

By means of the fifth column of table XVI the corrections to the absolute scale are found. Thus the tables XVI and XVIII enable us to reduce the temperatures calculated according to Comm. N°. 95*e* and used in Comm. N$^{os}$. 95*a*, 95*c* and 95*d* both to the normal hydrogen-scale and to the absolute scale.

For the temperatures in liquid hydrogen first the correction is to be applied which will prove to be necessary according to Comm. N⁰. 95*e* § 3*b* and § 8.

The temperatures $t_s$ occurring in Comm. N⁰. 97*a*, already corrected in the first column of table XVI for the application of the corrected pressure-coefficient 0.0036629 and the influence of the dead space, are adjusted to the absolute scale by the corrections in the fourth column of table XVI.

§ 3. The values found by CHAPPUIS and TRAVERS for the pressure-coefficient of hydrogen (cf. the footnote to § 7 of Comm. N⁰. 95*e*) are corrected to 0.00366266 and 0.00366297 (number of decimals the same as given by them.

For the pression-coefficient of carbonic acid found by CHAPPUIS the correction is more considerable and amounts (because the dead space is small here, the correction on account of the variation of density caused by expansion of the glass is here about of the same value as that on account of the variation of density by the dead space) to $- 0.25 \times 10^{-6}$, so that the value found by CHAPPUIS ¹) 0.00372624 is corrected to 0.00372599.

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¹) Nouvelles Etudes, Travaux et Mémoires du Bureau International. T. XIII, pag. 48.

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# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,
*Director of the Laboratory.*

## No. 98.

**Dr. H. KAMERLINGH ONNES and G. H. FABIUS.** "Repetition of DE HEEN's and TEICHNER's experiments on the critical state."

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## **Dr. H. KAMERLINGH ONNES and G. H. FABIUS**. "*Repetition of* DE HEEN'S *and* TEICHNER'S *experiments on the critical state*".

### § 1. *Introduction.*

Experiments have been repeatedly made from which the conclusion was drawn, that a substance can assume different densities above its critical temperature with the same pressure and the same temperature, which densities it can retain for hours according to some investigators [1]. That in reality this is not the case, and that the differences found are to be ascribed to admixtures or to differences in the pressure or the temperature of the phases compared appeared already when KUENEN (Comm. N°. 11, 1894) repeated GALITZINE'S experiments (Wied. Ann. 50, 1893), and found but trifling differences remaining. Afterwards when DE HEEN (Bull. Ac. Belg. 3e S. t. XXXI '96) had again found the differences of density in question by another way, it was shown by repetition of his experiments at Leiden (Comm. N°. 68, 1901), that also these differences of density vanish almost entirely for pure $CO_2$ when attention is paid to the differences of temperature. In the last few years, however, it has been particularly

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[1] TRAUBE Ztschr. f. phys. Chem. 58 p. 477. 1907, cf. also MATHIAS, Le point critique des corps purs p. 250.

When with change of density dissociations or variations of volume of the molecules themselves should make their appearance which clearly require more time than the establishment of temperature equilibrium through conduction of heat and convection, we should when a phase was kept at constant volume after having suffered variation of density, have to find an increase of the pressure both for liquid and vapour phases and for phases above the critical temperature; thermodynamically it follows from this that the density of liquid in equilibrium with vapour would then have to be a function of the time.

Cf. TRAVERS and USHER on variations of density in consequence of false equilibria.

TEICHNER's [1]) experiments that have given new support to the opinion that after all these differences of density really exist (DRUDE's Ann. 13, 1904).

In the first place we have repeated DE HEEN's experiment in different ways. Already with the earlier repetition (1901) thermo-elements had been introduced for the determination of the difference in temperature of the two metal reservoirs of the apparatus, which were separated by a cock, the apparatus for the rest resembling that of DE HEEN as closely as possible. One of the thermo-elements, however, was damaged during the experiments. Though it could be ascertained that the differences in density even without correction for the temperature were considerably smaller than those found by DE HEEN, probably on account of the greater purity of the $CO_2$, the exact amount of the difference remaining after temperature correction could not be determined. To replace these measurements by better ones, a new, improved apparatus with thermo-elements was built, resembling for the rest DE HEEN's apparatus as closely as possible, and with this apparatus we made the observations communicated in § 3 They confirm that the differences in density derived by DE HEEN from his experiments do not exist for a pure substance when temperature and pressure are uniform [2]).

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[1]) In the TEICHNER's tube the same differences of density which GALITZINE and WILIP (Congr. Intern. de Physique I 668, 1900) had found were shown by GILBERT-FARADAY's density-bulbs. What holds for TEICHNER's experiments applies therefore also to those of GALITZINE and WILIP.

[2]) So if there exist processes as meant in p. 3 note 1, they pass so quickly that it is not possible to demonstrate them by methods which require that the equilibrium of pressure and temperature has first been established. As yet nothing has been found that points to the fact that the establishment of the temperature equilibrium is retarded an appreciable time on account of changes of energy which increase in course of time to a definite limiting value, the volume remaining constant.

It was demonstrated in Comm. N°. 68 that admixtures and differences of temperature lead to systematic disturbances as in DE HEEN's experiments. Both give rise to disturbances of the same character. In the discussion of the influence of the differences of temperature the valuable paper by VILLARD Ann. d. Ch. et d. Phys (7) 10 (1897) has been overlooked there. That TEICHNER's results might be ascribed to small admixtures has appeared in details from the calculations by VERSCHAFFELT (Comm. Suppl. N°. 10, 1904).

To the influence of admixtures on phenomena in the neighbourhood of the

Further we have repeated Teichner's experiment [1]) with more precautions than had been taken by this observer. Especially a thermo-element (platinum-platinum-iridium not to sacrifice the security which the glass apparatus offers for the preservation of the purity of the substance) was adjusted in the upper and in the lower end of the Teichner tube, just as in de Heen's modified apparatus, to enable us to follow the differences of temperature in the tube [2]). By using $CO_2$ for the experiment, a high degree of purity could be reached, and we came into a region where the temperature could be kept constant up to a very small amount.

If we wish to prevent diffusion between the higher phases and the lower ones, the modified Teichner tube (at least when not a capillary constriction has been made in it [3])) is inferior to the modified apparatus of de Heen. Moreover when we wish to reach the equilibrium of temperature quickly, the bad conductivity of heat of the glass is a drawback, but it has the great advantage, that the changes of density can be observed at the same time with the other phenomena for the critical state. With regard to these phenomena Travers and Usher (Ztschr f phys. Chem. 57, p 365, 1906) and Young (ibid p. 262) published important papers, after we had made the experiments mentioned in § 7. In the main points our observations agree with the descriptions given by

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critical point attention has also been drawn by Young, Journ. de Chim. Phys. 4 (1906) p. 475. To this may be added that Keesom, Comm. No. 88, 1903 p. 74 did not only consider the inreasse of the pressure during condensation with constant temperature as a proof of the presence of admixtures, but that it served him further to arrive at an opinion on the quantity of the admixture.

[1]) This was already mentioned Comm. Suppl. No. 10, 1904. Lately Traube strongly urged the advisability of a repetition.

[2]) In a Cagniard-Latour tube thermometers were fused by Villard. Our tube may just as well be called a Villard tube with density-bulbs as a Teichner tube with thermo-elements.

[3]) Such an apparatus, if necessary provided with a valve which is worked magnetically might be serviceable in the investigation of the variation of density with temperature. [After this was printed in the Dutch Proceedings of the Academy we noticed that the device of a capillary constriction was used by Ramsay, Proc. Roy. Soc. 30 (1880) p. 327.]

TRAVERS and USHER and by YOUNG, and supplement them by giving the variations of the densities.

After what the repetition of DE HEEN's experiments had taught us again about the asserted differences of density at the same pressure and the same temperature above the critical temperature, our repetition of TEICHNER's experiments has become rather a first contribution to the study of the variations of density with temperature and pressure by this way, than a refutation of the conclusions derived from TEICHNER's experiments. We have, however, been able to show sufficiently by our experiments that these conclusions are erroneous.

§ 2. *Repetition of one of* DE HEEN's *experiments* As we can refer to Comm. n$^0$. 68 with regard to the choice of the experiment which is to be repeated (on account of the systematic character of the deviations only one need be repeated), and as on another occasion a full description of the apparatus used and the different operations will be given, we think that the following remarks on the arrangement of the experiments will suffice here.

1. The pure carbonic acid was prepared by distillation. The admixtures are to be estimated at no more than 0.00027 (cf. KEESOM Comm. N$^0$. 88 II, § 2 and V § 10). In the apparatus it comes into contact only with metal, glass, and cork (packings of this gave a perfect closure after having been repeatedly tightened during a week).

2. The apparatus, the conduits, and the further auxiliary arrangements, among which also two metal bottles with the purified $CO_2$, are all in connection with a mercury vacuumpump. One of the bottles with pure $CO_2$ serves for rinsing. From the second the desired quantity is conveyed into the apparatus by distillation.

3. The density in every reservoir is determined by making the carbonic acid flow from it into a large reservoir with mercury manometer kept at constant temperature. In the volumenometric calculations the corrections are applied according to the empiric equation of state V s. 1 of Comm. N$^0$. 74 (Arch. Néerl. (2) 6, 1901). Errors in the density caused by leakages in the

reservoirs at high pressure are excluded. It was ascertained by separate control experiments that the total amount of $CO_2$ in the apparatus remained unchanged during the experiments.

4. The apparatus was kept at uniform constant temperature by means of flowing water, a xylene thermoregulator (see Comm. N°. 70 III § 3) and a valve stirrer (see Comm. N°. 83 III § 4). Sufficient precautions were taken to prevent conduction of heat from outside to parts of the apparatus.

### § 3. *Variations of density found in the repetition of the experiment of* DE HEEN *after correction of the difference in temperature of the reservoirs.*

DE HEEN brings the temperature of the two reservoirs (see § 2 beginning) from 28° to about 35° C, and opens the cock between them 6 times four seconds during the heating; then when the temperature has become constant at about 35°, he opens the cock once more 6 times 4 seconds. Then he assumes that temperature and pressure are the same in the two reservoirs.

When repeating the experiment (being very careful to prevent drops from being scattered from one reservoir into the other) we found confirmed by reading the thermo-elements (nickel-iron), what was observed in Comm. N$^0$. 68 viz. that every time when the cock between is opened for adjustment of pressure, a difference of temperature arises between the two reservoirs, and that when closing the cock at the end of the experiment a difference of temperature remains, which must be taken into account.

In order to find out in how far the equilibrium of temperature and pressure has been reached, we have in the first place made three determinations, in which the cock was opened respectively 2, 4, and 6 seconds every time (probably our cock allowed comparatively less substance to pass than that of DE HEEN). The results have been given in the following table: $v$ denotes the upper, $l$ the lower reservoir, so $\rho_l$ is the density in the lower reservoir; the numbers of times the cock was opened during the heating (distributed over 15 minutes) and then at constant temperature (distributed over half an hour) have been separately given; $\rho'_l$ is $\rho_l$ corrected for $t_v - t_l$.

## SERIES I.

| Establishment of the equilibrium by opening the cock | $\rho_v$ | $\rho_l$ | $\rho_l / \rho_v$ | $t_v$ | $t_v - t_l$ | Corrected for difference of temperature | |
|---|---|---|---|---|---|---|---|
| | | | | | | $\rho'_l$ | $\rho'_l / \rho_v$ |
| 6 times 2 + 6 times 2 sec. | 0.418 | 0.506 | 1.21 | 34°.25 | 0°.27 | 0.456 | 1.09 |
| 6 times 4 + 6 times 4 sec. | 0.424 | 0.495 | 1.17 | 34.40 | 0.22 | 0.454 | 1.08 |
| 6 times 6 + 6 times 6 sec. | 0.427 | 0.489 | 1.15 | 34.20 | 0.16 | 0.456 | 1.07 |
| 6 times 6 + 6 times 6 sec. | 0.437 | 0.501 | 1.15 | 34.30 | 0.20 | 0.466 | 1.07 |

The temperature corrections have been borrowed from the graphical representation derived in Comm. N°. 68 from AMAGAT's determinations. The uncertainty which still prevails with respect to the correct course of the isotherms in the neighbourhood of the critical state is, of course, also found in these corrections.

The rather rapid process of the heating from 28° to 35° prevents further that the whole apparatus has already assumed the temperature of the waterbath, so that also the observed differences of temperature themselves are not quite certain.

In the following series of determinations we proceeded in the same way till the 12th opening (the 6th at constant temperature). It was put off for 3 hours. When the cock was opened the course of the deviations of the galvanometer appeared to be the same as in the preceding series; the remaining temperature corrections, however, were somewhat smaller than in the 1st series, which we ascribe to this that all parts of the apparatus have had time to assume the temperature of the waterbath. An increase of pressure in the lower reservoir, which should have been found when e. g. in this lower reservoir molecules were dissociated during these three hours (see § 1, p. 4 footnote 2 ), and which should have given rise to a greater galvanometer deviation when the cock was opened for the last time, could not be traced. We found:

## SERIES II.

| Establishment of the equilibrium by opening the cock | $\rho_v$ | $\rho_l$ | $\rho_l/\rho_v$ | $t_v$ | $t_v-t_l$ | Corrected for difference of temperature | |
|---|---|---|---|---|---|---|---|
| | | | | | | $\rho'_l$ | $\rho'_l/\rho_v$ |
| 6 + 5 + 1 time 2 sec | 0.430 | 0.497 | 1.16 | 34°.55 | 0°.20 | 0.466 | 1.08 |
| 6 + 5 + 1 time 4 sec. | 0.440 | 0.489 | 1.11 | 34.85 | 0.16 | 0.456 | 1.04 |
| 6 + 5 + 1 time 6 sec. | 0.439 | 0.485 | 1.10 | 34.40 | 0.15 | 0.452 | 1.03 |

In virtue of what the preceding determinations had taught us as to the reaching of equilibrium of temperature and pressure the cock was opened 12 times 12 seconds in a following determination, and finally two more determinations were made in which the cock was opened 12 times 4 seconds and at last once five minutes. We found:

## SERIES III.

| Establishment of the equilibrium by opening the cock | $\rho_v$ | $\rho_l$ | $\rho_l/\rho_v$ | $t_v$ | $t_v-t_l$ | Corrected for differences of temperature | |
|---|---|---|---|---|---|---|---|
| | | | | | | $\rho'_l$ | $\rho'_l/\rho_v$ |
| 6 + 6 times 12 seconds | 0.446 | 0.488 | 1.09 | 34°.70 | 0°.20 | 0.456 | 1.02 |
| 6 + 6 times 4 sec. | 0.427 | 0.445 | 1.04 | 34.05 | 0.06 | 0.432 | 1.01 |
| at last 5 minutes | 0,462 | 0.478 | 1.03 | 34.00 | 0.06 | 0.467 | 1.01 |

From this follows that as the equilibrium of pressure and temperature is obtained better, the densities of the phases become more and more equal, and that at last after the application of the temperature correction only very small differences remain.

*The much more considerable* deviations found by DE HEEN

($\rho_l/\rho_v = 1.19$, see Comm. No. 68) must, therefore, be attributed to admixtures and differences of temperature [1] [2].

§ 4. *Example of differences of density as found by* DE HEEN *caused by a slight impurity of the $CO_2$.*

The great influence of small quantities of admixture is very convincingly shown by the following results.

In a group of determinations ending with a repetition of experiment 2 Series I we found:

| Establishment of the equilibrium by opening the cock | $\rho_v$ | $\rho_l$ | $\rho_l/\rho_v$ |
|---|---|---|---|
| 6 + 6 times 4 sec. | 0.392 | 0.531 | 1.35 |

It appeared that in consequence of carelessness in the cleaning after it had been repaired, in the metal bottle in which the pure carbonic acid was kept, a trace of oil had been left which had diffused in the carbonic acid When we thought that the whole apparatus had been sufficiently cleaned by blowing pure carbonic acid through it, we found:

| Establishment of the equilibrium by opening the cock | $\rho_v$ | $\rho_l$ | $\rho_l/\rho_v$ |
|---|---|---|---|
| Only 6 times 4 sec. during the rise of the temperature. | 0.385 | 0.555 | |
| 6 + 3 times 4 sec. | 0.399 | 0.521 | 1.30 |
| 6 + 6 times 4 sec. | 0.417 | 0.505 | 1.21 |

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[1] That during the opening of the cock no important exchange of liquidogeneous and gasogeneous molecules (to use the terminology of DE HEEN) between the upper and the lower reservoir can have taken place, appears from this, that when the upper reservoir was filled with air and the lower reservoir with air with 31 pCt. $CO_2$, and the equilibrium was established without the cock being opened, after the cock had been opened for 5 minutes, only 0.33 percent of $CO_2$ had passed into the upper reservoir.

[2] They give both systematic errors of the same character (cf. § 1 p. 4 note 1).

which by the side of Series I and II gives at the same time an idea with what degree of approximation equilibrium of pressure is reached by the repeated opening of the cock. Repeating the last determination after continued blowing we found:

| | | | |
|---|---|---|---|
| 6 + 6 times 4 sec | 0.426 | 0.496 | 1.19 |

The last observation harmonizes pretty well with Series I N⁰ 2, of which it is a repetition, the same deflections of the galvanometer being moreover found. It leads to the same $\rho'_l/\rho_v$.

It appears how misleading even the presence of slight impurities may be, and that in Comm. N⁰. 68 the leather packings have been justly called a fundamental defect of DE HEEN's apparatus (cf. 1 § 2 above).

§ 5. *Correction for gravity and for slight admixtures in the experiment of* DE HEEN. *Result.*

In order to be able to calculate the correction which is to be applied to $\rho'_l/\rho_v$ for gravity, we must know the density as function of the level in a column of pure $CO_2$. The accurate shape of the isotherms in the critical state being very uncertain ¹), this function is not accurately known. GOUY has taken SARRAU's equation of state as basis for his calculation. We have started from the equation of state V s. 1 of Comm. N⁰. 74. Only 0,0002 was found for the correction at 34° and 8 c.M. difference of level, so that it may be neglected. As to the correction for the admixtures for the $CO_2$, when we put their amount as given in § 2, at 0,00027, it becomes 1°/₀ à 1,5°/₀ at 34°.5 C. according to the calculations of VERSCHAFFELT, Comm. Suppl. N⁰. 10. If the uncertainty of this correction is taken into account, we must come to the conclusion, the limit of accuracy of our experiments not being higher than 1°/₀ either, that the differences of density derived by DE HEEN from his experiments do not exist for pure $CO_2$ when sufficient care is taken to ensure equilibrium of pressure and temperature.

§ 6 *Repetition of* TEICHNER'S *experiment.* An elaborate descrip-

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¹) It is just to the knowledge of this shape that observations as made in § 3 and § 7 may contribute.

tion of the apparatus and the operations will be given on another occasion. Here the following remarks may suffice:

1. Repetition with $CO_2$ was considered to be desirable also by Teichner because it gives more warrants for purity.

2. A platinum-platinum-iridium thermo-element (used with a magnetically protected galvanometer of DuBois) was successfully fused into Teichner's tube at the top and at the lower end, so that the tube remained proof against a pressure of 150 atmospheres. However we did not succeed in making the thermo-elements free from disturbing electromotive forces, nor did they give with certainty the accuracy of 0°.01 we wished. The places of contact were found at $^1/_4$ and $^3/_4$ of the height of the tube. A third thermo-element to compare the temperature in the tube with that in the bath would be desirable.

3. The critical density of $CO_2$, 0.469 [1]), being smaller than that of $CCl_4$, with which substance Teichner worked, it was much more difficult to obtain the required density-bulbs (small glass bulbs) of 0.365, 0.390 and 0.405. We owe them as well as the fusion of the thermo-elements into the glass to the skill of Mr. O. Kesselring, chief of the glassblowing department of the laboratory. By means of Clebsch's formula it was found that the decrease of volume of the bulbs at the highest pressures can only amount to from $^1/_{600}$ to $^1/_{400}$.

4. Still greater care was devoted to the purification of the $CO_2$ than in the repetition of de Heen's experiment. From a metal bottle of $CO_2$ as used for the latter $^1/_3$ is once more blown off, and then $^1/_3$ distilled over into a second bottle from which under weighing, so much is suffered to escape that a fixed quantity remains. This second bottle is connected by glass tubes with the experimental tube, a mercury manometer, a mercury vacuumpump and an auxiliary bottle (also of metal) with pure $CO_2$ for rinsing the conduits, after which the fixed quantity which it contains, is quite distilled over into the experimental tube, the latter being immersed in liquid air; at last the experimental tube, still immersed in liquid air, is connected with the mercury vacuumpump, and fused

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[1] Derived by Keesom Comm. N°. 88 p. 52, from his observations by means of the rule of the rectilinear diameter.

off. By weighing it is ascertained that the desired quantity has been transferred to the experimental tube.

5. A mode of heating which does not give rise to convection currents inside the tube, is considered of great importance also by TEICHNER and TRAUBE, to prevent mixing of what is at the upper end and what is at the lower end of the tube. TEICHNER does not accept YOUNG's refutation of his experiments (see TEICHNER, loc. cit.) because in YOUNG's apparatus convection currents are not so well prevented as in that of himself. The thermostat used by us, however, satisfies much higher demands than that of TEICHNER. The tube is immersed in a liquid bath in a double walled non-silvered vacuumglass wich is hermetically closed with a badly conducting lid. The glass is provided with a valve-stirrer and an arrangement to heat the bath electrically from above, and is itself again immersed in a bath with double glass walls, which is likewise provided with a valve-stirrer. With the exception of two windows, the space between these two walls is filled with cotton wool, by which the outer wall too is surrounded. Like the bath in which the improved apparatus of DE HEEN (§ 2) was placed, the outer bath was kept at constant temperature (up to 0.°02) by flowing water with the aid of a xylene thermoregulator (§ 2). In this way the temperature of the bath in which the experimental tube is, can be kept constant up to 0.°002. The heating takes place according to the indication of thermometers divided into 50th of a degree, which are placed in the inner and in the outer bath, and is regulated in such a way that everything that might give rise to convection currents is as much as possible avoided.

6. When manipulated the tube was always efficiently shielded for the protection of the observer.

§ 7. *Observations.* The bulbs correspond with the densities 0.365, 0.390, 0.405, 0.421, 0.443, 0.450, 0.466, 0.483 and 0.510.

The position of the bulbs and that of the meniscus (indicated in what follows by the read number of the mark of division between [ ]) was read on a millimeter scale etched on the tube; in the middle of the tube the mark 30 is found, the zero point is 20 mm. above the bottom.

In the *first experiment* the heating took place very slowly; at

first also the inner bath was (electrically) heated, $t_e$ refers to the outer bath, $t_i$ to the inner one. After three hours small gas bubbles were seen to rise from the downmost thermo-element, probably caused by conduction of heat along the wires in consequence of $t_e$ having increased too much. We observed:
June 29 1906.

| time | $t_e$ | $t_i$ | men. | |
|---|---|---|---|---|
| $11^h$ | 27°.8 | 27°.15 | [31] | |
| 11 30 | | 27.92 | | |
| 12 20 | | 30 00 | | |
| 12 25 | 30.4 | 30.39 | | the rising of the gas bubbles has finished, the bulbs begin to show a tendency to divide |
| 12 30 | | 30.69 | | 0.365 rises |
| 12 33 | | 30.83 | | 0.365 at 33 |
| 12 36 | | 30.88 | [33] | 0.510 begins to descend slowly to 25 |
| | | 30.94 | | 0.510 at 5 |
| | | 30 99 | | 0.510 on the bottom |
| | | | | the separate (electrical) heating of the inner bath is stopped. |
| 12 40 | 31.00 | 31.00 | | 0.365 at 36.<br>0.483 begins to descend |
| 12 44 | | 31.00 | [34] | 0.365 between 38 and 39<br>0.483 „ 21 and 22 |
| | | | | $t_i$ rises very slowly whereas $t_e$ was all the time kept some what higher untill $2^h.50$ |
| 12 48 | | | | 0.483 between 10 and 11<br>0.365 rises to the top with accelerated motion<br>0.483 continues to descend very slowly |
| 12 52 | | | [34.5] | 0.483 has arrived at the bottom<br>all except 0.510, 0.483, and 0.365 in meniscus |
| 1 | | | [35] | 0.390 begins to rise |
| 1 3 | | | | 0.390 between 37 and 38 with 0.405 by its side somewhat lower |
| 1 10 | | | | 0 390 between 38 and 39 with 0.421 below it in a slanting direction |
| 1 15 | | | [35] | 0.421 begins to rise, for the rest like $1^h10'$. |

Looking from the top downward in a slanting direction through the tube we observe a slight grey mist which is denser in the part below the meniscus. When we look straight through the tube, with a light behind the tube, the whole shows a light brown colour, which is somewhat darker under the meniscus.

The bulbs continue to move slowly apart, the rising ones moving faster than the descending ones, and the velocity of the rising bulbs increasing as they get higher, the same thing taking place though in a smaller degree with the descending ones.

$2^h15$ 31.032 the meniscus has gradually got fainter and is hardly to be distinguished, only a slight constriction of the light band is to be perceived at 35

2 20 31.036 0.421 between 42 and 43
0.443 „ 36 and 37
0.450 „ 34 and 35
0.466 „ 32 and 33

2 50 31.22 the outer bath is further kept at this temperature

2 50 31.050 the rise of the temperature of the inner bath is now exceedingly regular

4 30 31.096 0.443 in the middle of 53
0.450 between 32 and 33
0.466 „ 24 and 35

The mist in the tube is now equally dense everywhere, and becomes gradually less, the moving apart of the three still descending bulbs continues slowly and regularly

8 7 31.210 0.466 lies just on the bottom
0.450 between 36 and 37; has risen 4 mm in $2^h15'$ and so shows a tendency to move to the top.

8 10 The cooling takes place by reducing the outer bath to a lower temperature

8 30 31.133 0 466 begins to rise from the bottom
0.450 at the same place

8 35 Throughout the tube a bluish mist appears

8 40 This mist gets denser

8 50 At [15] a thick milky white mist is formed, which spreads rapidly upwards and downwards.

30.984 At [10] the meniscus appears. From the upper place of contact of the thermo-elements drops fall down, from the lower place of contact smaller gas bubbles rise upwards. (The cooling proceeds too rapidly). The meniscus rises, 3 bulbs fall quickly into it from above, and 1 rises towards it from the bottom.

The differences of temperature within the tube were found to be between 0°.02 and 0° 03, but in consequence of disturbances they were often not to be observed. In the observation of $8^h7$ they were no more than 0°.01.

July 5 1906.

In the *second experiment* the heating took place somewhat more rapidly. In $1^h10'$ the inner bath was brought at

$9^h10'$ 29°.99 The separation of the bulbs has, of course, not advanced so far as in the first observation, and the deflections of the galvanometer were larger. The tube remained now farther behind the temperature of the waterbath.

9 40 31.60 [36] The meniscus is still dimly to be distinguished here, and a thin light mist is visible through the whole tube. Under the meniscus a somewhat darker band of a light brown colour is seen.

The position of the bulbs is now
0.365 at the top
0.390 between 43 and 44
0.405 „ 42 and 43
0.421 in the middle 41
0.443 „ „ „ 40
0.450 „ „ „ 39
0.466 between 37 and 38
0.483 and 0.510 on the bottom.

31.7 0.390 and 0.405 now go very rapidly to the top followed by 0.421.

At the place of the meniscus now only a slight constriction and a light brown mist band are to be perceived.

10 45 31.900 The temperature is then kept constant till

$11^h37$ with no greater deviation than 0°.004 and then from

11 37 31.888 till $2^h15$ with no more deviation than 0°.002.

2 15 The mist has now entirely vanished and the bulbs are all apart.
0.510, 0.483, 0.466 on the bottom
0.450 and further ones in the top, none of the bulbs remain suspended in the body of the tube; the bulb 0.450 was the last to go to the top, whereas 0.466 had already been on the bottom for some time.

A difference of temperature is no longer to be perceived.

At first the cooling took place more slowly.

3 31.550 A slight mist is perceived

3 45 31.040 the mist has become distinctly denser.

5 10 30.985 [5]. In this position the menicus originates in a milky cloud in the lower part of the tube. Further the lowering of the temperature proceeds too rapidly.

5 25 30.950 [14]. Three bulbs float in the meniscus.

A disturbance in the regulation of the temperature of the outer bath puts a stop to the experiment.

July 11th 1906.

A *third experiment* did not give any difference with the first with slow heating. The temperature was kept still closer to the critical, and the heating went still more slowly. Now the meniscus descended, and the brown colour under the meniscus was particularly pronounced, it was darkest just below the meniscus, and gradually faded downward. After a slow heating which extended over $10^1/_2$ hours the meniscus disappeared at

$6^h$ 30°.986. The position of the bulbs was now
0.443 between 34 and 35
0.450 in the middle 27
0.466 between 25 and 26.

In consequence of a slight disturbance in the regulation of the outer bath $t_i$ descended to

6 45 30.984 [25] the meniscus appears, the position of the highest bulb does not undergo any change, the two others 0.450 and 0.466 float in the meniscus

9 15 31.010 the meniscus disappeared somewhat lower, the brown colour in the lower half is much more intense, at last it contracted to a dark brown band of ± 1 mM. width just below the meniscus. Gradually it grew lighter and shortly after the meniscus it also disappeared;

0.443 between 41 and 42
0.450 . . . . . 23 and 24
0.466 in the middle 22.

The temperature at the top of the tube was 0°.01 higher than at the bottom.

§ 8. *Conclusions and remarks.* An elaborate discussion of the observations in connection with other peculiarities of the net of isotherms in the neighbourhood of the critical state (cf. Comm. N°. 74 and Comm. N°. 88 IV § 5 and Comm Suppl. N°. 10), and as to those on the mist in connection with the observations of GOUY, TRAVERS and USHER and YOUNG [1]), must be deferred to a later occasion. However some conclusions are obvious.

As the temperature rises more slowly and the equilibrium in the tube is better reached, we can get nearer to equality of density of the vapour and liquid phases. We think we found a smaller difference in density in our measurements than any of the observers before us [2]).

We did so in the third experiment. The critical temperature was then fixed between 30°.984 and 30°.986 [3]). That at 30°.984

---

[1]) This includes the discussion of the mist stage of VON WESENDONCK, which would constitute the transition stage in the neighbourhood of the critical state, and which in any case can only extend over a small part of the region of density and temperature where a mist can be seen.

[2]) YOUNG, Journ. Chem. Soc. 71 (1897) p. 455 stated at 0°.05 below the critical temperature a difference of 14$^0/_0$ between the liquid and vapour densities.

[3]) The readings of the temperature have been reduced to those on a thermometer which had been controlled with an air thermometer accurate up to 0°.01 by the Phys. Tech Reichsanstalt. Our result agrees with that of KEESOM, 30°.98 (Comm. N°. 88 see above), made with the same thermometer. Moreover, besides and after the determinations of the critical temperature of $CO_2$ cited in LANDOLT-BÖRNSTEIN-MEYERHOFFER'S Phys. Chem. Tables are to be mentioned: VERSCHAFFELT Zitt. Versl. Juni '96 (31°.0), VON WESENDONCK Verh. d. Deutsch. Phys. Ges. 5. p. 238 (30°.95), BRINKMAN Diss. Amsterdam 1904 (31°.12).

only a small difference in density existed between liquid and vapour appears as follows. When the meniscus appeared we found 0.443 for the density of the vapour at the height 35. So we estimate the density at 0.452 at the height of the meniscus (25) according to the correction of § 5 (doubtful); bulb 0.450, however, floats on the meniscus. The density on the bottom is $< 0.483$ (height (see § 7 beginning) 5 cm. under 30), so we estimate the density of the liquid at 0.468 at the height of the meniscus; bulb 0.466 floats. Vapour and liquid differ, therefore, certainly less than $^1/_{10}$, and probably no more than $^1/_{20}$ in density. In the first experiment we found $\rho_v > 0.421$, $\rho_l < 0.483$ from which $\rho_v > 0.430$, $\rho_l < 0.468$ follow with the estimated correction for gravity; so under these less favourable circumstances a difference of less than $^1/_{10}$ is most likely realized. These results concerning the closer and closer approach of the density of liquid and vapour, which quite agree with the views of ANDREWS-VAN DER WAALS, deprive the much larger differences of phases at the same temperature and pressure above the crritical temperature, which TEICHNER derives from his experiments, of all importance[1]).

It is in harmony with this that a tolerably sharply defined critical density can be assigned. We derive 0.460 from the density of vapour and liquid in the third experiment for it, which agrees with the mean which would follow from experiment 1 at $2^h15$, i.e. 0.450, and 0.470, derived from experiment 3 on account of the appearance of the meniscus at 25 (cf. further § 6 p. 12 footnote 1).

Differences of density as TEICHNER finds, were also found by us; it was in the second experiment at the moment that the meniscus disappears with comparatively rapidly rising temperature. However, after the tube has been kept at the same temperature above the critical temperature for 3 hours, and the temperature in the tube 0°.9 above the critical temperature has become uniform probably up to less than 0°.01, they have been reduced to less than 0.466—0.450, or less than 3.5°/$_0$, i.e. after correction for gravity $<$ 3.3°/$_0$ over 10 cm.

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[1]) It is true we might assume that the equilibrium of liquid and vapour with so slight a difference of density as we observed, is only reached after so long a time as was allowed in this experiment to obtain equilibrium of temperature, and that at first states with greater difference of density of liquid and vapour (cf. note 1 p. 3 § 1) appear at the same temperature, which gradually pass into the final state with simultaneous change of the pressure of coexistence (cf. note 1 p. 3 § 1) But the absence of subsequent rise of pressure in the repetition of DE HEEN'S experiment (see § 3) has taught us, that already after a very short time afterchanges of the density no longer occur.

The remaining difference in the first experiment 0°.23 above the critical temperature after 6 hours heating above the critical temperature can be derived from the fact that bulb 0.450 floats 5.6 cm. above 0.466. This difference is no more than 3.5°/$_0$ and corrected for gravity 2.9°/$_0$.

From VERSCHAFFELT'S calculations follows that at 0° 23 above the critical temperature 0.0001 molecule of admixture may cause about 12°/$_0$ difference of density. Differences of temperature and admixtures which may account for remaining differences such as those just treated are scarcely to be avoided even with the precautions taken by us.

Nothing has been observed of an "Entmischung" by cooling when the critical temperature is approached, as TRAUBE l.c. p. 477 mentions.

TEICHNER observed that, after the disappearance of the meniscus, at the place where it was found last a transition zone exists towards which the differences of density concentrate, whereas outside it the changes are only insignificant. In our observations the contrary appeared, and the changes in density continue regularly with increase of temperature, only the motion of the bulbs was slightly accelerated as they approach the top of the tube, and they cover the last 1 or 2 cm. very rapidly. In a less degree but in the same way this takes place with the bulbs which descended. We consider these phenomena to be connected wiht heating and cooling of phases by compression and expansion [1]).

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[1]) They just as the "Entmischung" assign that the temperature differences within the tube in the experiments of TEICHNER were probably greater than in ours.

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

## No. 99a.

**Dr. H. KAMERLINGH ONNES and C. BRAAK.** "Isotherms of diatomic gases and their binary mixtures. VI. Isotherms of hydrogen between —104° C. and —217° C." (*Continued*).

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam* **29 Juni 1907** p. 162—164).

EDUARD IJDO — PRINTER — LEIDEN.

**Dr. H. KAMERLINGH ONNES and C. BRAAK.** "*Isotherms of di-atomic gases and their binary mixtures.* VI. *Isotherms of hydrogen between* — 104° C. *and* — 217° C." (Continued).

§ 14. *Survey of the determinations.*

The determinations mentioned in this Communication constitute one whole with those of Communication N°. 97*a*. They may partly serve to control the earlier determinations at — 104° and — 136°, which, being the oldest observations, are not quite so reliable as the others. For the determinations of isotherms at lower temperatures they are a valuable supplement for the smaller densities from 70 to 100 times the normal one. With the exception of the isotherm of — 217° the determinations communicated till now may be considered as a whole. To complete this set of determinations a part of the isotherm mentioned for the density at about 170 times the normal one is still wanting. We hope soon to publish the additional determinations referring to this. To the standard-temperatures at which we determined the isotherms, we have still added — 164° C. From the data mentioned in Comm. N°. 97*a* may be derived (see § 13 of the communication mentioned) that the point where the inclination of the *pv*-curve for exceedingly small densities becomes zero, is close to this temperature. The purpose of the determinations at — 164° is to determine this point, which we shall call the *Boyle-point*, more definitely.

The determinations, with the exception of that at — 140°, were made at temperatures very near to the standard-temperatures of Comm. N°. 97*a*. They may be reduced to these standard-temperatures by a simple correction (See Comm. N°. 97*a* § 6). This reduction has not yet been carried out for the isotherms mentioned below. In Table XIX the temperatures are given at which the measurements were made. They were determined and calculated in exactly the same way as those of Comm. N°. 97*a*; just as to these latter temperatures the correction of Table XVIII Comm. N°. 97*b* is still to be applied to them.

We may still remark about the measurement of the pressure (cf. § 3), that for the lowest pressures a direct connection with the open manometer was required, because the auxiliary closed manometer cannot be used below 20 atms

### § 15. *Remarks about the manometers and the piezometers.*

When the determinations were finished, the auxiliary manometer was once more compared with the open standard-manometer. It proved that the normal volume had again undergone a slight diminution, viz. of 0.00026 of the original value. This comparison was made at about 22, 28 and 55 atmospheres. If the calculations of the pressure are carried out with the corrected normal volume, the remaining differences between the indications of the open and the closed manometer are smaller than $\frac{1}{10000}$ of the total pressure.

The steeltube $f_4$ with hexagonal portion $f_5$ on the stem of the piezometer $b_5$ (cf. fig. 2 Pl. II Comm. N°. 69, for the details at the top of the tube compare fig. 4 ibid. $f_1$, $f_2$, $f_4$) was soldered to the glass stem $b_5$ in the way described in Comm. N°. 94*b*. Now the packing could be pressed down more tightly (cf. § 4 Comm. N°. 97*a*) without danger of the block sliding from the stem.

The dimensions of the different parts of the piezometer were about the same as in the determinations of series I of Comm. N°. 97*a*. The glass stem had a greater length and a volume of about 12 cm$^3$., which enabled us to determine a greater part of the isotherms than was possible in series I. The reservoir had the somewhat smaller volume of 5.1583 cm$^3$.

### § 16. *Second group of values of $pv_A$.*

In table XIX the results of the determinations have been given in the same way as in Table XII of Comm. N°. 97*a*.

In conclusion we express our hearty thanks to Mr. J. Clay for his valuable assistance in this investigation.

TABLE XIX. $H_2$. Series IV. Values of $pv_A$.

| N⁰. | $t$ | $p$ | $pv_A$ | $d_A$ |
|---|---|---|---|---|
| 1 | −103°.71 | 28.423 | 0.63208 | 44.967 |
| 2 | | 38.154 | 0.63648 | 59.944 |
| 3 | | 48.682 | 0.64143 | 75.897 |
| 4 | | 58.317 | 0.64628 | 90.222 |
| 5 | −139°.88 | 25.432 | 0.49452 | 51.428 |
| 6 | | 33.774 | 0.49697 | 67.960 |
| 7 | | 41.273 | 0.49967 | 82.600 |
| 8 | | 48.558 | 0.50232 | 96.667 |
| 9 | | 25.380 | 0.49466 | 51.308 |
| 10 | −164°.14 | 22.818 | 0.40065 | 56.952 |
| 11 | | 28.688 | 0.40164 | 71.427 |
| 12 | | 34.387 | 0.40253 | 85.427 |
| 13 | | 39.947 | 0.40376 | 98.936 |
| 14 | −183°.18 | 20.409 | 0.32562 | 62.677 |
| 15 | | 24.705 | 0.32550 | 75.898 |
| 16 | | 28.374 | 0.32521 | 87.248 |
| 17 | | 32.416 | 0.32522 | 99.673 |
| 18 | | 20.400 | 0.32557 | 62.663 |
| 19 | −195°.17 | 18.554 | 0.27867 | 66.581 |
| 20 | | 23.337 | 0.27765 | 84.055 |
| 21 | | 27.879 | 0.27622 | 100.933 |
| 22 | −204°.69 | 16.752 | 0.24040 | 69.684 |
| 23 | | 20.456 | 0.23880 | 85.658 |
| 24 | | 24.019 | 0.23695 | 101.367 |
| 25 | −212°.82 | 15.416 | 0.20644 | 74.679 |
| 26 | | 18.038 | 0.20430 | 88.296 |
| 27 | | 20.643 | 0.20228 | 102.051 |
| 28 | −217°.40 | 14.638 | 0.18742 | 78.103 |
| 29 | | 16.787 | 0.18495 | 90.766 |
| 30 | | 18.857 | 0.18293 | 103.080 |

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BY

PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory*

## No. 99$^b$.

**Dr. H. KAMERLINGH ONNES and J. CLAY.** "On the measurement of very low temperatures. XVI. Calibration of some platinumresistance thermometers."

(On the measurement of very low temperatures. XV. is to be found in Comm. No. 97*b*).

(*Translated from : Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam* **29 Juni 1907** p. 165—168).

EDUARD IJDO — PRINTER — LEIDEN.

## **Dr. H. KAMERLINGH ONNES and J. CLAY.** "*On the measurement of very low temperatures.* XVI. *Calibration of some platinum-resistance thermometers.*"

§ 1. *Introduction.* The investigation on the variation of the resistance of metals (pure ones and those with known admixtures) set on foot many years ago (see Comm. N°. 77 § 1, 1902) at Leiden, comprises besides the determination of the galvanic resistance of conductors made of the different metals, also the determination of the expansion for each of these metals. We have only little advanced as yet with the latter part of this investigation, the expansion has only been investigated for platinum, which was chosen as standard metal, and then only down to — 182° [1]). We hope shortly to publish a Communication on the expansion down to — 252° C. For the present, however, the knowledge of this expansion is not yet of much importance for the investigation of the variation of the specific resistance with the temperature. When in this investigation we descend to very low temperatures, the correction for the expansion becomes so small compared with the disturbance in consequence of other influences which are still further to be investigated, that we may disregard it for the moment.[1]

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[1]) In Comm. N°. 85 (1903) it was remarked for the first time that in order to represent the expansion of glass from — 180° to 0° a formula of the second degree with other constants was required than for the range from 0° to + 100°. We found this confirmed in Comm. N°. 95*b* (June '06), and also applicable to platinum, for which a formula of the third degree, as we gave one for glass, proved necessary between — 180° and + 100°. Afterwards (Dec. '07) SCHEEL, who was at first (Zeitschr. f. Instr.k. April '06) of opinion that a formula of the second degree could be found for platinum between — 190° and + 100°, came to the same opinion as we, and gave the three constants for platinum. Our formula of the second degree for platinum between 0° and — 180° quoted by SCHEEL was used by us to prove, that for platinum between — 180° and + 100° a formula of the second degree is *not sufficient*, but that a formula of the third degree is required. In order to show this with given values at + 100°, 0° and – 190° observations at a temperature about halfway between 0° and — 190°, as our — 87°, are more suitable than observations at a temperature between 0° and + 100°, as those by SCHEEL at + 56°.

The investigation consists then in the calibration of different resistance thermometers. The wires treated in this Communication being chiefly of importance to us as resistance thermometers, we have inserted their calibration in this series.

§ 2. *Particulars on the comparison and on the investigated wires.* In these calibrations we have taken the platinum wire which was compared with the hydrogen thermometer in Comm. N⁰. 95*c* (June '06) and which we shall call $Pt_I$, as standard. We determined the variation of the resistance of the other wires by bringing them together with $Pt_I$ at the desired temperature, and by then comparing their resistance with that of $Pt_I$. The two platinum wires $Pt_{III}$ and $Pt_V$ were brought in the same cryostat (see § 4 Comm. N⁰. 95*c*) together with $Pt_I$, and whereas the temperature was kept constant with one resistance according to the indication of the WHEATSTONE-bridge, the ratio of the resistance of the other to $Pt_I$ was determined by means of the differential galvanometer. $Pt_V$ was also measured separately with the WHEATSTONE-bridge. The difference of the results by the two methods amounted only to 0 02 % at the lowest temperatures[2].

Just as $Pt_I$, $Pt_{III}$ and $Pt_V$ were supplied by HERAEUS; they were delivered at the same time, but later than $Pt_I$. The diameter of all three was 0.1 m.m. After having been treated and wound round the glass (see Comm. N⁰. 95*c* § 3) in the same way, they were heated for a long time in an annealing furnace for glass. $Pt_{III}$ and $Pt_V$ differed only in this respect that after being heated $Pt_V$ was partly unwound, and then wound again, and was not heated in the annealing furnace again.

To obtain also a resistance thermometer of very small dimensions a platinum wire of 0.05 m.m. diameter was wound round a tube of 1 c.m. diameter and about 8 c.m. long. The thin platinum wire was welded to thick platinum wires which were fused in the glass. Consequently the thermometer could be cleaned by means of acids if necessary. The thin wire $Pt_d$ used for this thermometer, was also furnished by HERAEUS.

---

[1] Here it is left entirely undecided whether the variation of the resistance with the temperature is not in close connection with the expansion.

[2] The values at 0° were $Pt_{III} = 160.111\ \Omega$ and $Pt_V = 151.139\ \Omega$.

A fourth wire was investigated to get an idea of the

§ 3. *Invariability of the resistance thermometers for low temperatures with the time*, viz. the resistance thermometer with which the observations were made by MEILINK in 1902, and which we shall call $Pt_M$. The zero point appeared to have remained unchanged to one 30000th 1). This was also the case with $Pt_I$, after measurements had been made at very low temperatures with the resistance thermometer for two years

Repetition of the calibration at low temperatures of 1902 did not give an equally good harmony. We found:

TABLE IV 2).

| Hydrogen th. | 1902 | 1907 | Deviation in Ω | Deviation in ° C. |
|---|---|---|---|---|
| 0° | 110.045 | 110.048 | — 0.003 | |
| —182.63 | 28.692 | 28.605 | + 0.087 | + 0°.25 |
| —197.08 | 21.877 | 21.999 | — 0.022 | — 0.05 |
| —209.93 | 16.025 | 15.934 | + 0.089 | + 0.25 |

We think that we cannot draw another conclusion from it than that the reliability of the measurements with the hydrogen thermometer in 1902 was not yet so great as it has become now as appears from Comm. No. 95*d*.

§ 4. *Results.* The measurements have yielded for the resistance of each of the wires expressed in that at 0° as unit:

---

1) The thermometer had got defect in consequence of the bursting of the glass cylinders. However carefully it was repaired, yet this gave rise to a diminution of length of the wire of 3 m m. or 0.039 %, for which a correction was applied.

2) The tables in this Communication are numbered in succession to table III of Comm. N°. 95*d*.

## TABLE V.[1]

Comparison of different platinum resistance thermometers.

| Temperature. | $Pt_I$ | $Pt_{III}$ | $Pt_V$ | $Pt_M$ | $Pt_d$ |
|---|---|---|---|---|---|
| 0° | 1. | 1. | 1. | 1. | 1. |
| — 30.53 | 0.87890 | 0.87860 | 0.87798 | | |
| — 58.56 | 0.76693 | 0.76652 | 0.76640 | | |
| — 87.54 | 0.64984 | 0.64923 | 0.64927 | | |
| — 87.92 | | 0.64776 | | | |
| —103.83 | 0.58346 | | | 0.58720 | |
| —109.09 | 0.56204 | 0.56034 | 0.56127 | | |
| —140.21 | 0.43313 | 0.43201 | 0.43182 | | |
| —159.11 | 0.35370 | 0.35245 | 0.35206 | 0.35979 | |
| —182.79 | 0.25283 | 0 25154 | 0.25098 | 0.26022 | 0.27374 |
| —195.11 | 0.20043 | 0.19900 | 0.19856 | 0.20808 | 0.22294 |
| —204.68 | 0.15974 | 0.15819 | 0.15880 | | 0.18355 |
| —212.18 | 0.12814 | 0.12653 | 0.12626 | 0.13630 | 0.15293 |
| —216.65 | 0.11016 | 0.10854 | 0.10824 | | |
| —216.80 | | 0.10797 | | | |
| —252.82 | 0.01421 | | | | 0.040637 |
| —255 18 | 0.01244 | | | | 0.03766 |
| —258.86 | 0.01072 | | | | 0.03652 |

It appears that wires delivered at the same time show the same course with only small deviations. A considerable difference in deformation of the wire has had only a slight influence for

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[1] By the application of small corrections (cf. Comm. No. 101*a* § 4) these values slightly differ from those given in the Proceedings of the Roy. Acad.

$Pt_V$. The great difference with wires delivered at different times points to the fact that the originally used material and the treatment in drawing the wires out decide on the change of the resistance. How great the influence of the treatment in drawing is appears from the comparison of $P_{III}$ and $Pt_d$. They were supplied by HERAEUS about the same time and are therefore probably made of platinum of the same degree of purity. Yet the thinner wire $Pt_d$ decreases much less in resistance than the thicker one. At the temperature of liquid hydrogen the differences become very large. In view of the results obtained for gold, which have been inserted in the following Communication (N°. 99*c*), the most plausible explanation is this that the admixtures in the platinum of the wires sent by HERAEUS, either due to their being less pure by nature or to the way of drawing, were less with the platinum sent later than with that sent earlier. We come back to this in Comm. N°. 99*c*. Here we may still mention that DEWAR's wire gave 0.30521 at — 182°, whereas ours 0,25344, and that only the thickest (0.2 m.m.) of HOLBORN's wires gave a smaller value than ours, viz. 0 21253 at — 191°, whereas ours 0 21786.

§ 5 *Calibration formulae for the new wires.* Just as for $Pt_I$ we have also calculated the constants for each of the wires $Pt_{III}$ and $Pt_V$ in a calibration formula which is adjusted down to — 217° and does not give too great deviations at the hydrogen temperatures To be adjusted to the hydrogen temperatures too formulae of another form are required. The above mentioned formulae of the form $(A)$:

$$\frac{W_t}{W_0} = 1 + at.10^{-2} + bt.10^{-4} + ct.10^{-6} + d\left(\frac{10^2}{T} - \frac{10^2}{(273.09)^2}\right)$$

give for the adjustment which we distinguish by $A^I$:

| $A_I$ | $a$ | $b$ | $c$ | $d$ |
|---|---|---|---|---|
| $Pt_V$ | + 0.401819 | + 0.0007403 | + 0.0052641 | + 0.020666 |
| $Pt_{III}$ | + 0.398291 | — 0.0026645 | + 0 0039442 | + 0.016843 |

The mean error proved to be greater, for $Pt_V$ even considerably greater than in the calibration in Comm. N°. 95*c*, which can be ascribed only partly to the indirect method of the determination of the resistance.

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PROF. DR. H. KAMERLINGH ONNES,

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## No. 99c.

**Dr. H. KAMERLINGH ONNES and J. CLAY.** "On the change of the resistance of the metals at very low temperatures and the influence exerted on it by small amounts of admixtures."

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam,* **29 Juni 1907** p. 169—177).

EDUARD IJDO — PRINTER — LEIDEN.

## **Dr. H. KAMERLINGH ONNES and J. CLAY.** „*On the change of the resistance of the metals at very low temperatures and the influence exerted on it by small amounts of admixtures*".

§ 1. *Introduction.* In Comm. N°. 99*b* we called attention to the very large differences in the change of the galvanic resistance with the temperature, which different platinum wires show when we descend to the low temperatures which are to be reached with liquid hydrogen. Such differences were still more pronounced for different gold wires which we investigated. With this metal (see Comm. N°. 95*d* June 1906) we had taken in hand the investigation of the influence of small amounts of admixture announced in Comm. N°. 77, because the influence of admixing silver would probably be important and the percentage of silver could be determined very accurately, the possibility of drawing out wires of the different kinds of gold and its high melting point moreover rendering this metal preferable to the for the rest very suitable mercury.

Besides, the inquiry into the influence of small amounts of admixture on the change of the resistance of gold with the temperature proved at once useful as we thought that the gold resistance thermometer would be preferable to the platinum resistance thermometer. Dr. C. Hoitsema, who already obliged us before (see Comm. N°. 95*d*) by putting pure gold at our disposal, has had the kindness of supplying us again with different samples of gold of high purity, further of preparing for us different alloys with accurately known small percentages of admixture, and of determining the impurity which was finally left in the wires after they had been melted down. For all this valuable help and for the information which Mr. Hoitsema was enabled to give us by his wide experience we express our hearty thanks.

The investigation of the different gold wires with very small amounts of admixture may of course also be considered as the calibration of different gold resistance thermometers (Comp. Comm. N°. 99*b* § 1). We prefer, however, to consider it as a part of our more general investigation (Comm. N°. 77) on the change of the resistance with the temperature for pure metals, and on the influence which small amounts of admixture exert on it.

As to the change of the specific resistance for the pure metals reduced to the most normal state, attention is drawn to the temperature of the *point of inflection* $\frac{d^2r}{dT^2}=0$, the temperature of the *point of proportionality* $\frac{dr}{dT}=\frac{r}{T}$, and the temperature of the *minimum* $\frac{dr}{dT}=0$ It is clear that the situation of these points and the correspondence [1]) and difference of their situation and of the coefficient of variability of the resistance with the temperature in general for different metals of different classes must furnish important data for the theory of electrons.

The investigation of these points is only possible by the aid of liquid hydrogen. Only in some cases — and even then the purity of the metal is open to doubt — the point of inflection, whose existence was indicated by Dewar, was found high enough to be ascertained without measurements for hydrogen temperatures. For metals in the purest and normal state the point of proportionality lies probably still below the temperatures which are to be reached with liquid hydrogen. It is true that Dewar derived from his measurements at two hydrogen temperatures that it was surpassed for some of his metal wires. Our measurements, however, point to this that as a metal is brought to a purer and more normal state, the point of proportionality is found to be lower. The metal wire which came nearest to this *ideal* state, was one of our gold wires. Even at the lowest temperature the point of proportionality was not yet reached for that wire. Probably DEWAR'S wires were further removed from this ideal state.

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[1]) In this respect something is to be derived from the formulae given by us in this and in the preceding communications.

With the low situation which we find for the point of proportionality measurements at two hydrogen temperatures do not suffice, but we have made determinations at at least three hydrogen temperatures, because they were necessary to determine the probale situation of the point of proportionality by the aid of $\frac{d^2r}{dt^2}$. Until we have reached the point of proportionality, we need not discuss the question of the minimum point.

In the inquiry into the properties of the metals in the ideal state we must know first of all in how far the metal is in this state, and else how we can derive what would be found in this state. The influence of small deviations in the nature of the metals on the change of the resistance with the temperature, becomes so exceedingly great for the hydrogen temperatures, that a special investigation is necessary for them. Here two things have to be paid attention to: to small amounts of admixture, and to differences in hardness etc For the present we have left the latter out of account; in the investigation of the influence of the admixtures, however, the influence of the hardness was as much as possible eliminated by our treating the different samples of metals exactly in the same way when comparing them, and by reducing them to the same state of softness.

The most natural explanation of the whole of the results obtained as yet (in this and the preceding Communication) is to ascribe the deviations for the different wires of one and the same metal to impurities in the metal, which may also come in during the drawing if efficient precautions do not prevent it, and which even in very small quantities exert a very great influence on the changes of the resistance with the temperature.

The influence of the drawing is altogether lost for mercury, in which it is also easy to ensure uniform distribution of small quantities of admixture. This enhances the importance of the study of this metal for the investigation of the influence of admixture In the first place we have measured its resistance at hydrogen temperatures, at which it had not yet been determined;

it is given in § 4. It proved that for pure mercury the inflection point falls in the region of liquid hydrogen temperatures [1]. This is a drawback for the inquiry into the change of the resistance with the temperature for pure metals.

Just as the gold wire $Au_V$ (see § 2), also the silver wire $Ag_I$ and the platinum wires of the preceding Communication are probably purer than DEWAR's wires of the same metals. For bismuth, on the other hand, DEWAR has most likely had a purer sample than we. The change of the resistance at hydrogen temperatures for this metal, which had not yet been measured by him, has been given in § 5. The observations for lead for those temperatures, which were still wanting up to now, have been given in § 6.

The high degree of purity for some of the metals which were at our disposal, and the lower temperatures to which we descended (solid hydrogen evaporating at 2.5 m.m. pressure) render the decrease of the resistance in some cases many times larger than was observed by DEWAR. To this it is also to be ascribed that we have noted the great influence, which very small changes in the nature of the metal obtain on the change of the resistance at hydrogen temperatures. We may account for this by paying attention to the difference of the resistance of a wire of pure metal at the temperature $T$, $r_{iT}$, with that of a wire of the same metal with a proportion of admixture $x$ at the same temperature, $r_{xT}$. According to a theorem of MATTHIESSEN [2] derived from observations between 0° and 100°, this difference (the theorem refers to a difference that is about the same as that considered here) is constant for different temperatures. FLEMING [3] found this theorem about confirmed down to — 200°. As we have found, this theorem no longer holds for hydrogen temperatures. But the deviation is not of such a nature as to affect our conclusions. So if to form an idea of the influence of the admixtures, we put $r_{xT} = r_{iT} + px$, further $p$ constant and large, then it is clear that

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[1] Perhaps in connection with the low melting point. Possibly the point of proportionality is first reached for osmium.

[2] Pogg. Ann. Bd. CXXII.

[3] Proc. Royal Institution June 1896 p. 9.

— when $r_{iT}$ becomes as small as is the case (see Table I $Au_V$) for pure metals at hydrogen temperatures — the resistance of a metal for the case that $x$ gets an appreciable amount, is to be ascribed almost exclusively to the admixture. The small amounts of admixture obtain a remarkable influence [1]).

Analogies are easily found in the important influence of small amounts of admixture on the density in the neighbourhood of the critical temperature of a substance, in a space becoming opaque by a cloud depositing on a mininum quantity of dust. But for a further discussion the systematic investigation of the influence of small amounts of admixture should be more advanced. At all events the changes of the resistance with temperature at hydrogen temperatures proves to be a highly sensitive criterion to decide about the nature of a metal.

§ 2. *Gold.* The different samples of pure gold were all supplied by Dr. C Hoitsema. With the exception of two the wires were all treated in exactly the same way, drawn out by Heraeus to 0.1 mm. diameter, and treated at every pull with diluted sulphuric acid and nitric acid. The gold wire $Au_{VI}$ was drawn in a different way and thereby made strongly impure. The exact amount has not yet been ascertained. $Au_0$ is the wire which was calibrated in Comm. N°. 95*d*. After melting it down Dr. Hoitsema found 0.03°/₀ impurities. As to the wires $Au_{III}$, $Au_{IV}$ and $Au_V$, Dr. Hoitsema found about 0.015°/₀ admixture for $Au_{III}$, about 0.005°/₀ admixture for $Au_{IV}$ and $Au_V$. $Au_{AgI}$ was made of an alloy which after the wire had been remelted, contained 0.4°/₀ admixture (probably chiefly silver). Wound round the same glass cylinder all wires except $Au_0$ and $Au_{AgI}$ were heated at the same time in an annealing furnace for

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[1]). To a less degree of purity of the examined metal wires it is perhaps to be ascribed that Niccolai, Att. Linc. 16, 1st sem. p. 906 finds a smaller decrease of resistance at — 189° than we do, as appears by comparison with Tables I, III, V of this communication and V of Comm. N°. 96*b*. Indeed Niccolai finds:

| | silver | gold | lead | platinum |
|---|---|---|---|---|
| 0° | 1 | 1 | 1 | 1 |
| — 189° | 0.2784 | 0.3068 | 0.3357 | 0.3198 |

a long time, and slowly cooled, as had also been done with $Au_0$ and $Au_{AgI}$, so that they were perfectly malleable.

In table I the resistances have been given expressed in that at 0° as unit. These were about 9Ω.

### TABLE I.

Change of the resistance of different Gold wires with the temperature.

| Temperature. | $Au_{III}$ | $Au_{IV}$ | $Au_V$ | $Au_{VI}$ | $Au_0$ | $Au_{AgI}$ |
|---|---|---|---|---|---|---|
| 0° | 1. | 1. | 1. | 1. | 1. | 1. |
| −103.83 | 0.59601 | 0.59389 | 0.59306 | 0.64827 | 0.60545 | 0.64549 |
| −183.00 | 0.27653 | 0.27177 | 0.27096 | 0.37053 | 0.30070 | 0.37099 |
| −197.87 | 0.21456 | 0.20963 | 0.20871 | 0.31659 | 0.23908 | |
| −205.01 | | | 0.17897 | | 0.20992 | |
| −215.34 | 0.14058 | 0.13407 | 0.13337 | 0.16822 | 0.16681 | |
| −252.93 | 0.01602 | 0.008743 | 0.008103 | 0.13669 | 0.04554 | 0.13942 |
| −255.13 | | | 0.005691 | | | |
| −258.81 | 0.01095 | 0.004265 | 0.003601 | 0.13241 | 0.03982 | 0.13288 |
| [−261] | | | 0.002713 | | | |
| [−262] | | 0.003257 | 0.002526 | | | |

To facilitate comparison we may observe that DEWAR found 0.03290, whereas we found 0.008103 at — 252°.93 for $Au_V$.

§ 3. *Mercury.* It was doubly distilled and brought into a glass spiral. The latter was protected by a bath of pentane, which was slowly cooled from the bottom upwards before it was immersed into the bath of the cryostat. We found:

### TABLE II.

Change of the resistance of pure Mercury with the temperature.

| Temp. | Resistance. |
|---|---|
| 0° | 97.126 |
| — 183.00 | 7.2650 |
| — 197.87 | 6.0103 |
| — 205.01 | 5.3900 |
| — 215.34 | 4.5057 |
| — 252.93 | 1.2613 |
| — 258.81 | 0.7534 |

§ 4. *Silver.* This was also supplied by Dr. C. HOITSEMA and drawn to a wire of 0.1 m.m. by HERAEUS, during which operation it was

### TABLE III.

Change of the resistance of Silver with the temperature.

| Temperature | Resistance $Ag_I$ | $O-C_D$ | $O-C_{A_{VI}}$ |
|---|---|---|---|
| 99°.76 | 1.41089 | 0 | 0 |
| 0 before | 1. | 0 | 0 |
| 0 after | 1.00037 | | |
| — 103.81 | 0.58087 | — 0.00042 | — 0.00042 |
| — 139.87 | 0.43282 | + 42 | + 42 |
| — 183.57 | 0.24679 | — 17 | 0 |
| — 195.17 | 0.19703 | + 29 | — 2 |
| — 204.67 | 0.15528 | — 31 | |
| — 252.92 | 0.008913 | 0 | |
| — 259.22 | 0.006942 | 0 | |

treated in exactly the same way as the gold and the platinum. After the resistance had been determined, the composition was controlled; the silver contained then 0.18°/₀ impurity. The zero point of the silver wire (resistance at 0°) changes slightly by being drawn out in consequence of the difference in expansion of silver and glass. The preceding table gives the resistance expressed in that at 0° as unit. (The resistance at 0° was 21.519 Ω).

Column $O-C_D$ contains the deviations from a formula adjusted from + 100° to — 259° of the new form:

$$\frac{Wt}{W_0} = 1 + at \,.\, 10^{-2} + bt^2 \,.\, 10^{-4} + ct^3 \,.\, 10^{-6}$$

$$+ d\left(\frac{10^6}{T^3} - \frac{10^6}{(273.09)^3}\right) + e\left(\frac{10^{10}}{T^5} - \frac{10^{10}}{(273.09)^5}\right) \,.\,.\, (D)$$

which agreed best with the values:

| $D$ | $a$ | $b$ | $c$ | $d$ | $e$ |
|---|---|---|---|---|---|
| $Ag_I$ | +0.402746 | +0.004355 | +0.004806 | +0.00955 | —0.000013 |

For a comparison with platinum and gold the column $O-C_{A_{IV}}$ gives the deviations from a formula of the form $A$ (see Comm. N°. 95*c* and 95*d*):

$$\frac{W_t}{W_0} = 1 + at\ 10^{-2} + bt^2 . 10^{-4} + ct^3 . 10^{-6} + d\left(\frac{10^2}{T} - \frac{10^2}{273.09}\right)$$

with values which we distinguish by $A_{IV}$ on account of the other way of adjusting the coefficients.

| $A_{IV}$ | $a$ | $b$ | $c$ | $d$ |
|---|---|---|---|---|
| $Ag_I$ | +0.40355 | +0.03968 | +0.005232 | +0.008662 |

§ 5. *Bismuth.* The measured resistance, which we shall also investigate in the magnetic field, was that of a bismuth spiral of Hartmann and Braun N°. 301. The resistance expressed in that at 0° as unit (the resistance at 0° was 17.3138 Ω) was:

### TABLE IV.

Change of the resistance of Bismuth with the temperature.

| Temperature | Resistance $Bi_I$ | $O-C_{A_{III}}$ |
|---|---|---|
| 12°64 | 1.05148 | 0 |
| 12°70 | 1.05165 | |
| 0 | 1 | |
| — 103.71 | 0.63649 | + 0.00952 |
| — 139.88 | 0.52865 | — 127 |
| — 164.05 | 0.46246 | — 144 |
| — 182.73 | 0.41435 | — 69 |
| — 195.17 | 0.38478 | + 144 |
| — 204.68 | 0.36064 | + 127 |
| — 216.01 | 0.33014 | — 69 |
| — 253.01 | 0.22329 | — 92 |
| — 255.34 | 0 21388 | — 2 |
| — 258.86 | 0.19574 | 0 |

This column $O-C_{A_{III}}$ gives the differences with a formula of the form $A$ (see § 4), with values which we shall indicate by $A_{III}$ on account of the adjustment at two hydrogen temperatures and over the region to 0°:

| $A_{III}$ | $a$ | $b$ | $c$ | $d$ |
|---|---|---|---|---|
| $Bi_I$ | +0.399037 | +0.051928 | +0.0038155 | —0.0079700 |

§ 6. *Lead.* The knowledge of the resistance of lead is of particular importance on account of the fact that this metal does not show the Thomson-effect Probably the lead used by us, contained no more than $0.015\,^{0}/_{0}$ admixture

The resistance of a narrow strip cut out from the flatted lead and protected against chemical action by paraffine expressed in the resistance at 0° (3.18114 Ω) as unit was found to be:

TABLE V.

Change of the resistance of Lead with the temperature.

| Temperature | Resistance |
|---|---|
| + 16°.33 | 1.0652 |
| 0° | 1 |
| —103.63 | 0.59548 |
| —183.65 | 0.29439 |
| —195.15 | 0.25257 |
| —204.52 | 0.21742 |
| —216.61 | 0.17129 |
| —252.78 | 0.03032 |
| —255.07 | 0.02314 |
| —258.70 | 0.01311 |

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

## No. 100a.

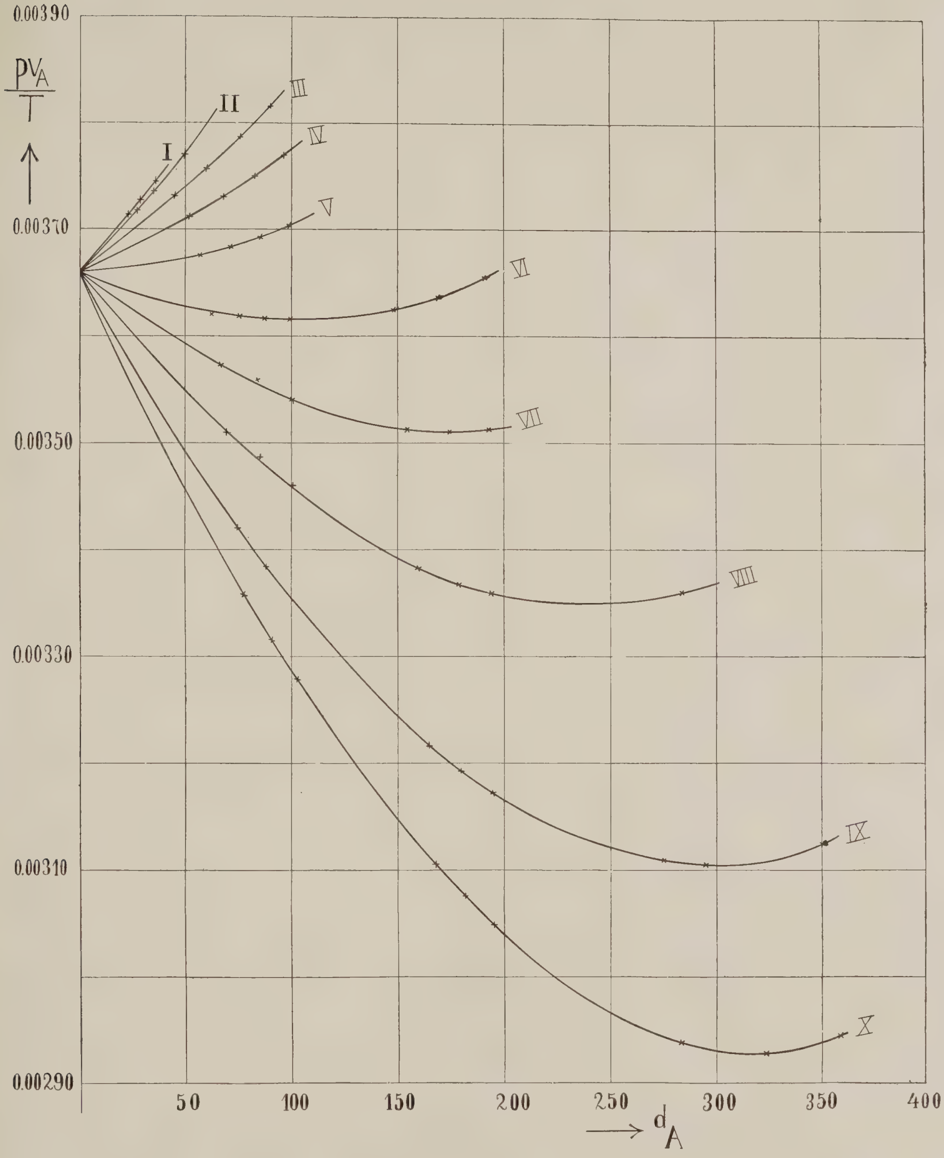
**Dr. H. KAMERLINGH ONNES and C. BRAAK.** "Isotherms of diatomic gases and their binary mixtures. VI. Isotherms of hydrogen between —104° C. and —217° C." *(Continued)*. (*With a plate*).

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam*, **30 November 1907**, p, 411—417).

Eduard IJdo — Printer — Leiden.

Dr. H. KAMERLINGH ONNES and C. BRAAK. "Isotherms of diatomic gases and their binary mixtures. VI. Isotherms of hydrogen between — 104° C. and −217° C." (Continued).

PLATE I.



Communication No. 100a.

**Dr. H. KAMERLINGH ONNES and C. BRAAK.** "*Isotherms of diatomic gases and their binary mixtures.* VI. *Isotherms of hydrogen between* —104° C. *and* —217° C." (Continued).

## § 17. *Survey of the determinations. Remark on the apparatus.*

The measurements mentioned in this Communication comprise in the first place the supplementary determinations to which we already alluded in § 14 of Comm. N°. 99*a* (June 1907). These are three determinations at — 217° at a density of about 170 times the normal one.

The obvious thing to do further was to repeat the other determinations of series II with the same piezometer arranged for the determinations mentioned above, this piezometer being one of about the same dimensions as that of series II of Comm. N°. 97*a* (December 1906). As a matter of fact a comparison of the values of $pv_A$ obtained in this series with those yielded by the series III and IV teaches that the former lie somewhat, though only slightly, lower than the latter. This may be due to a systematical error as the filling in the later series was accomplished with more precautions (compare § 5 of Comm. N°. 97*a*). In the series now given, just as in series IV, distilled hydrogen was used.

Both the steel tubes on the stem of the piezometer and those on the stem of the piezometer reservoir were soldered to the glass (cf. § 15 of Comm. N°. 99*a*). This ensures a gas-proof connection with the steel capillary. With sealing wax it is difficult to make the connection gas-proof, because sometimes the nut begins to slide off when the flange is tightly screwed on.

## § 18. *Values of $pv_A$ of series* V.

In table XX the results of the determinations have been represented in the same way as in table XII of Comm. N°. 97*a*. The temperatures at which the measurements were made, were —182°.74, —195°.16, —204°.62, —212°.91 and —215°.94. In table XX the reduction to the standard temperatures of table XII has been carried out. It was effected by interpolation by means of virial coefficients, which were derived in § 12 of Comm. N°. 97*a*. This enabled us to abandon the elaborate method of § 8. The computation of the temperatures took place in the same way as in Comm. N°. 95*e*.

TABLE XX. $H_2$. Series V. Values of $pv_A$.

| N°. | $t_s$ | $p$ | $pv_A$ | $d_A$ |
|---|---|---|---|---|
| 1 | —182°.81 | 48.431 | 0.32746 | 147.90 |
| 2 | | 55.499 | 0.32857 | 168.91 |
| 3 | | 62.889 | 0.33028 | 190.41 |
| 4 | —195°.27 | 42.304 | 0.27362 | 154.61 |
| 5 | | 47.782 | 0.27351 | 174.70 |
| 6 | | 52.808 | 0.27360 | 193.01 |
| 7 | —204°.70 | 36.999 | 0.23165 | 159.72 |
| 8 | | 41.258 | 0.23061 | 178.91 |
| 9 | | 44.631 | 0.23001 | 194.04 |
| 10 | —212°.82 | 32.035 | 0.19414 | 165.01 |
| 11 | | 34.611 | 0.19270 | 179.61 |
| 12 | | 37.275 | 0.19149 | 194.66 |
| 13 | —217°.41 | 29.030 | 0.17318 | 167 63 |
| 14 | | 31.191 | 0.17152 | 181.85 |
| 15 | | 33.180 | 0.17005 | 195.12 |

§ 19. *Values of* $pv_A$ *of series* IV.

If in the same way as in the preceding § the results of table XIX of Comm. N°. 99*a* are reduced to the standard temperatures the values of the adjoined table are obtained. For — 139°.88 this reduction has not been carried out, as it is better to take this temperature as standard temperature instead of — 135°.71. Here the reduction would have to be made for a comparatively large difference

TABLE XXI. $H_2$. Series IV. Values of $pv_A$ .

| N⁰. | $t_s$ | $p$ | $pv_A$ | $d_A$ |
|---|---|---|---|---|
| 1 | — 103°.57 | 28.447 | 0.63261 | 44.967 |
| 2 | | 38.186 | 0.63702 | 59.944 |
| 3 | | 48.724 | 0.64198 | 75.897 |
| 4 | | 58.368 | 0.64694 | 90.222 |
| 5 | — 139°.88 | 25.406 | 0.49459 | 51.368 |
| 6 | | 33.774 | 0.49697 | 67.960 |
| 7 | | 41.273 | 0.49967 | 82.600 |
| 8 | | 48.558 | 0.50232 | 96.667 |
| 9 | — 164°.14[1] | 22.818 | 0.40065 | 56.952 |
| 10 | | 28.688 | 0.40164 | 71.427 |
| 11 | | 34.387 | 0.40253 | 85.427 |
| 12 | | 39.947 | 0.40376 | 98.936 |
| 13 | — 182°.81 | 20.496 | 0.32704 | 62.670 |
| 14 | | 24.818 | 0.32699 | 75.898 |
| 15 | | 28.506 | 0.32672 | 87.248 |
| 16 | | 32.568 | 0.32675 | 99.673 |
| 17 | — 195°.27 | 18.527 | 0.27827 | 66.581 |
| 18 | | 23.303 | 0.27724 | 84.055 |
| 19 | | 27.837 | 0.27580 | 100.933 |
| 20 | — 204°.70 | 16.749 | 0.24036 | 69.684 |
| 21 | | 20.453 | 0.23876 | 85.658 |
| 22 | | 24.015 | 0.23691 | 101.367 |
| 23 | — 212°.82 | 15.416 | 0.20644 | 74.679 |
| 24 | | 18.038 | 0.20430 | 88.296 |
| 25 | | 20.643 | 0.20228 | 102.051 |
| 26 | — 217°.41 | 14.635 | 0.18738 | 78.103 |
| 27 | | 16.784 | 0.18491 | 90.766 |
| 28 | | 18.853 | 0.18289 | 103.080 |

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[1] This temperature has been derived from the comparison of the resistance thermometer with the hydrogen thermometer of July 3, '07 (see table I, Comm. N⁰. 101*a*).

of temperature, and would become inaccurate. It is, therefore, preferable to leave the values of table XIX for this temperature intact, and if necessary apply the reduction to those of series I which are much less reliable. The temperature — 164°.14 has been adopted as new standard temperature.

The determinations 5 and 9 as well as 11 and 18 of table XIX have been united to a mean.

## § 20. *Comparison of the series* I *and* II *with the control determinations.*

For reasons mentioned in § 17 the points of series I and II have been determined twice in a mutually perfectly independent way. They can be easily compared with the control determinations of IV and V by reducing them to the same density and temperature by means of virial coefficients. If in this way for — 103°.57 Nos. 2, 3 and 4 of series I (see table XII) are compared with 1, 2 and 3 of series IV (see table XXI), we find for the differences of $pv_A$ for IV—I respectively:

+ 0.00001 , + 0.00007 , — 0.00019

and for —139°.88 for IV (5,6) — I (2,3):

— 0.00085 , — 0.00036.

Dealing in the same way with the series II and V (see tables XII and XX), we find respectively for the temperatures —182°.81, —195°.27, —204°.70, and —212°.82,

V (1, 2) — II (2, 3) = + 0.00007, + 0.00010
V (4, 5, 6) — II (2, 3, 4) = + 0.00012, + 0.00026, + 0.00017
V (7, 8, 9) — II (2, 3, 4) = + 0.00020, + 0.00019, + 0.00034
V (10, 11, 12) — II (2, 3, 4) = + 0.00013, + 0.00008, + 0.00021

The differences are to be ascribed chiefly to condensation of impurities, as they diminish with increase of the temperature. This was considered as sufficient ground to reject the results of the series I and II for the further calculations as less reliable. This was also done for —104°, though the series I and IV harmonize very well for this temperature. When we disregard the influence of the probable condensation the very regular course in the situation of the points is an indication about accuracy of the measurements themselves also for the other isotherms.

So there remain the determinations of the series III, IV and V, which, reduced to the standard temperatures, occur in the tables XII, XX and XXI. With these data the further calculations have been carried out. Plate I gives a survey of the situation of the points in the diagram of isotherms; on this plate $\frac{pv_A}{T}$ has been given as function of the density ($T$ absolute temperature). By I and II the isotherms of 100° 20, and 0°, which will be treated in the following communication, are indicated, by the other Roman figures ascending with decrease of temperature those to —217°.41.

### § 21. *Individual virial coefficients.*

In the same way as has been explained in § 12 of Comm. N⁰. 97*a* the first three virial coefficients of the development into series considered there were calculated for every isotherm by means of the earlier and the new data. They have been put together in the subjoined table.

TABLE XXII. $H_2$. Individual virial coefficients.

| $t_s$ | $A_A$ | $10^3.B_A$ | $10^6.C_A$ | $10^{12}.D_A$ | $10^{18}.E_A$ |
|---|---|---|---|---|---|
| — 103°.57 | 0.62048 | + 0.24409 | + 0.5300 | + 0.9113 | — 0.648 |
| — 139°.88 | 0.48765 | + 0.11175 | + 0.4034 | + 0.6753 | — 0.378 |
| — 164°.14 | 0.39891 | + 0.00732 | + 0.4148 | + 0.4970 | — 0.208 |
| — 182°.81 | 0.33063 | — 0.07947 | + 0.3908 | + 0.3809 | — 0.088 |
| — 195°.27 | 0.28508 | — 0.12309 | + 0.3165 | + 0.2892 | — 0.016 |
| — 204°.70 | 0.25074 | — 0.17328 | + 0.3398 | + 0.2166 | + 0.031 |
| — 212°.82 | 0.22103 | — 0.22271 | + 0.3599 | + 0.1514 | + 0.066 |
| — 217°.41 | 0.20424 | — 0.24539 | + 0.3558 | + 0.1122 | + 0.082 |

In the same way as in Comm N⁰. 97*a* the differences between the observed values of $pv_A$ and those calculated by means of the found virial coefficients are put together in a table, which we subjoin. The second column contains the differences for the points of the hydrogen thermometer (see table XII of Comm. N⁰. 97*a*), the following columns refer to the observations belonging to series IV, V and III, the different observations being arranged according to the ascending densities.

TABLE XXIII. $H_2$. Deviations from the formula.

| $t_s$ | $10^5 \; (O_i - C_i)$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| — 103°.57 | — 1 | + 8 | — 1 | —11 | + 6 | | | | | |
| — 139°.88 | — 2 | +13 | —15 | 0 | + 4 | | | | | |
| — 164°.14 | 0 | — 3 | + 7 | — 6 | + 2 | | | | | |
| — 182°.81 | — 1 | —15 | +13 | + 3 | +12 | —15 | — 9 | +12 | | |
| — 195°.27 | — 4 | — 2 | +25 | —11 | —16 | 0 | + 8 | | | |
| — 204°.70 | —18 | + 4 | +36 | +22 | —22 | —24 | —21 | +23 | | |
| — 212°.82 | —14 | + 3 | +12 | +22 | — 5 | —10 | — 4 | —22 | +18 | |
| — 217°.41 | —14 | +13 | 0 | +15 | — 2 | + 1 | — 3 | —22 | — 6 | +18 |

It appears that on the whole series IV gives higher values than series V. The calculated curves may serve for the adjustment of the series mutually. Undoubtedly their points will be more reliable than those of the separate determinations. In future we shall, therefore, start from the virial coefficients of XXII.

## § 22. *Minima of* $pv_A$.

With the now available data the minima of the $pv_A$-curves were now again determined for the lowest five temperatures, and as before the coefficients $P_0$, $P_1$ and $P_2$ of a parabola calculated. The columns of table XXIV have the same meaning as those of table XV of Comm. N⁰. 97*a*.

TABLE XXIV. $H_2$. Minima of $pv_A$

| $t_s$ | $pv_A$ | $d_A$ | $p$ | O—C |
|---|---|---|---|---|
| —182°.81 | 0.32663 | 99.70 | 32.57 | — 0.29 |
| —195°.27 | 0.27348 | 183.10 | 50.07 | + 1.36 |
| —204°.70 | 0.22945 | 238.27 | 54.67 | — 0.21 |
| —212°.82 | 0.18782 | 287.99 | 54.09 | — 0.84 |
| —217°.41 | 0.16342 | 321.51 | 42.54 | + 0.19 |
| | 0.39292 | 0 | 0 | —0.23 |

For the calculation of the coefficients of the parabola a sixth point was used which has been inserted at the bottom of the table and was obtained by means of the isotherm of — 164°.14. For this temperature the value of $B_A$ is very slight, and by means of interpolation the BOYLE-point can be easily determined. For this is found, measured on the absolute scale:

$$\theta = -165°.72 \text{ C},$$

to which corresponds a value of $pv_A = 0.39292$.

For the coefficients of the parabola we find:

$$P_0 = - \quad 14.8370$$
$$P_1 = + \quad 676.563$$
$$P_2 = - 1624.31.$$

The differences in the last column of table XXIV are slight, except for —195°.27. For this temperature $C_A$ appears also to be too small. Both deviations must be owing to the not quite accurate position of one or more of the points of the isotherms. From the diagram of Plate I it is already to be seen that the middle point of series IV probably lies too high.

The parabola cuts the ordinate $p = 0$ in two points where $pv_A$ is respectively $= 0.39330$ and $0.02323$, with which agree the absolute temperatures:

$$T_1 = 6.3 \quad , \quad T_2 = 107^\circ.5.$$

For the top of the parabola $pv_A = 0.20826$, with which corresponds a pressure of 55.61 atmospheres From this follows for the absolute temperature of the isotherm which passes trough the top:

$$T = 64^\circ.2.$$

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

## No. 100$^{b}$.

**Dr. H. KAMERLINGH ONNES and C. BRAAK.** "Isotherms of diatomic gases and their binary mixtures. VII. Isotherms of hydrogen between 0° C. and 100° C."

*(Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam,* **30 November 1907**, p. 420—430).

EDUARD IJDO — PRINTER — LEIDEN.

**Dr. H. KAMERLINGH ONNES and C. BRAAK.** "*Isotherms of diatomic gases and their binary mixtures.* VII. *Isotherms of hydrogen between* 0° C. *and* 100° C."

### § 1. *Survey of the determinations.*

The reservoir of 5 cm$^3$. of the piezometer of series IV (Comm. N$^0$. 99*a*, June 1907) was replaced by one of 10 cm$^3$. With this apparatus two isotherms were determined, one in ice and one in vapour of boiling water. To obtain constant temperatures the same instruments were used as in Comm. N$^0$. 60 (June 1900). The water manometer (cf. § 8 of Comm. N$^0$. 27 (June 1896)) was read, but the difference of pressure amounting to no more than 0.5 mM., the corresponding correction for the temperature might be neglected. For the determination of the temperature of the steel capillary 4 thermometers were suspended along it. For the determination at 100° a paper screen had been applied to turn off the rising current of heated air; the spiral with cold water, however, above the wool packing of the boiling apparatus, had been omitted. The difference of temperature between the thermometers amounting to no more than 2°, this was permissible.

The corrected indication of the aneroid barometer amounted to 765.4 mM., from which for the temperature of the boiling-point follows 100°.20.

### § 2. *Values of* $pv_A$.

In the subjoined table the results of the determinations have been represented. The columns have the same meaning as in table XIX of Comm. N$^0$. 99*a*.

TABLE I. $H_2$. Values of $pv_A$.

| No. | $t$ | $p$ | $pv_A$ | $d_A$ |
|---|---|---|---|---|
| 1 | 0° | 27.333 | 1.01511 | 26.926 |
| 2 | | 35.602 | 1.02002 | 34.903 |
| 3 | | 43.413 | 1.02505 | 42.352 |
| 4 | | 50.583 | 1.02964 | 49.127 |
| 5 | 100°.20 | 30.970 | 1.38619 | 22.342 |
| 6 | | 39.796 | 1.39143 | 28.601 |
| 7 | | 50.254 | 1.39788 | 35.951 |

## § 3. *Individual virial coefficients.*

As has been done in § 12 of Comm. No. 97*a* we may avail ourselves of the data of table I to derive the first two virial coefficients for every isotherm. On account of the small densities which occur in these measurements, in formula (1) of § 12 of Comm. N⁰. 97*a*, $D_A$, $E_A$ and $F_A$ have been put $= 0$, so that the formula reduces to:

$$pv_A = A_A + \frac{B_A}{v_A} + \frac{C_A}{v_A^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Only a small number of points having been given, and the densities being small, as was remarked before, $C_A$ cannot be determined with sufficient accuracy. We borrowed the values of this coefficient from Comm. N⁰. 71 § 3, where $C_{A_0} = 0.0_6670$ and $C_{A_{100}} = 0.0_6606$.

In order to determine the course of the $pv_A$-curves more accurately the value of $pv_A$ was chosen for a density corresponding to that in the hydrogen thermometer of Comm. N⁰. 60 with which 0.0036627 was found for the pressure coefficient of hydrogen at 1090 mm. zero point pressure. By successive approximations this value of $pv_A$ is to be derived by means of these determinations of isotherms. We find for 0°:

$$pv_{A\ 0°.1100\ \mathrm{mm.}} = 1.00026$$

and for 100°.20 with the pressure coefficient 0.0036627:

$$pv_{A\ 100°.2} = 1.36737.$$

For the density $d_A = 1.44$ may be put in both cases.

Now we obtain five values of $pv_A$ and $d_A$ for 0°, and four for 100°.20, from which by the method of least squares the coefficients $A_A$ and $B_A$ of equation (1) may be determined. These values are:

For 0°:

$$A_A = 0.99924$$
$$B_A = 0.5800 \times 10^{-3}.$$

For 100°.20:

$$A_A = 1.36626$$
$$B_A = 0.8632 \times 10^{-3}.$$

For 100°.00 we may calculate from this:

$$A_A = 1.36553$$
$$B_A = 0.8626 \times 10^{-3}.$$

The differences which remain between the values of $pv_A$ of table I and those calculated according to formula (1) with the coefficients found here are respectively:

for 0°:

$+$ 0.00018, $-$0.00023, $-$0.00028, $+$0.00004, $+$0.00029;

for 100°.20:

$-$0.00013, $+$0.00034, $-$0.00001, $-$0.00019.

The first value always refers to the point calculated for the hydrogen thermometer. The differences are slight, and do not or only very slightly exceed $\frac{1}{4000}$ of $pv_A$.

# COMMUNICATIONS
FROM THE
# PHYSICAL LABORATORY
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BY

PROF. DR. H. KAMERLINGH ONNES,
*Director of the Laboratory.*

## No. 101a.

**Dr. H. KAMERLINGH ONNES, C. BRAAK and J. CLAY.**
"On the measurement of very low temperatures. XVII. Determinations for testing purposes with the hydrogen thermometer and the resistance thermometer".

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam,* **30 November 1907**, p. 420—426).

EDUARD IJDO — PRINTER — LEIDEN.

**Dr. H. KAMERLINGH ONNES, C. BRAAK and J. CLAY.** "*On the measurement of very low temperatures.* XVII. *Determinations for testing purposes with the hydrogen thermometer and the resistance thermometer*".

## § 1. *Introduction.*

In communication N⁰. 95*e* (Oct. 1906) the results of a number of measurements are recorded which show the possibility of measuring temperatures down to — 217° with the hydrogen thermometer accurately to $\frac{1}{50}$ deg. The results obtained with several fillings showed that with our measurements to — 217° this accuracy has been reached indeed. It was our plan to make also the following measurements:

1st. more testing determinations between 0° and — 217° in order to establish still better the limit of the accuracy of the temperature measurements with the hydrogen thermometer and the accuracy of the definition ¹) once for all of special temperatures by definite resistances of a resistance thermometer;

2nd. the extension of the testing determinations to measurements in liquid hydrogen;

3rd. the determination of definite standard temperatures by means of the boiling points and melting points of hydrogen, oxygen and other substances that can be easily purified ²);

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¹) In investigations the reading of temperatures with a resistance thermometer will as a rule for simplicity be preferred to reading them with the hydrogen thermometer. In this Communication the resistance thermometer of Comm. N⁰. 95*c*, which is called $Pt_I$, was used.

²) When we possess the fixed points meant here, the hydrogen thermometer can for calibrations be replaced by boiling point apparatus filled with pure gas and placed in the same bath as the apparatus to be calibrated. This is a great simplification in cases where only these *few special* temperatures are required. Moreover in these fixed points we have the means for a comparison between gas thermometers filled with different gases (for instance $H_2$ and He) or between thermometers in different laboratories.

4th. (comp. Comm. N⁰. 95*a* § 1, June 1906) temperature measurements with the helium thermometer, *a.* for a direct or an indirect comparison with the hydrogen thermometer, *b.* in order to get a firm basis for the determination of the lowest temperatures, especially with a view to the reduction to the absolute scale.

The investigation mentioned sub 3 and 4 has advanced a good deal. We now intend to communicate some measurements relating to 1st and 2nd.

### § 2. *Survey of the determinations.*

With regard to the controls meant sub 2nd two independent determinations have been made with entirely the same apparatus for comparison. The measurements meant sub 1st did not entirely succeed owing to a small reparation which the resistance thermometer required [1]. These measurements, however, have thereby acquired a signification in another respect, namely as a new calibration from — 104° to — 259° of the resistance thermometer used in Comm. N⁰. 95*e*; they allow us to judge in how far after similar reparations, which in the long run will be inevitable, the same temperature coefficients will remain valid for the resistance thermometer.

The communicated measurements determine also with a greater accuracy a couple of temperatures (comp. however the note in § 3, 2°) which hitherto had not been determined with the desired reliability (comp. §§ 3 and 5) [2].

The results have been combined in a table following below. The second and third columns contain the readings of the hydrogen thermometer and of the resistance thermometer. Those of the hydrogen thermometer are calculated in the way of Comm. N⁰. 95*e* (designated by *t*). The next column shows the resistances of column 3 recalculated with the factor 1.01806, which is the ratio between the resistances at 0° C. before and after the breaking of

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[1] When the resistance broke, only $^1/_{60}$ of the wire was lost, yet on account of this one might allege that if the latter is not perfectly homogeneous variations in the coefficients of temperature are not entirely excluded. These are especially to be feared as a result of the new winding of the wire. The thermometer till now called $Pt_I$ was named $Pt'_I$ after the breaking of the wire.

[2] These measurements were already used in table V, Comm. N⁰. 99*b* (June 1907) at — 252°.82 and — 255°.18 instead of the deviating ones of table I, Comm. N⁰. 95*c* (June 1906).

For insertion in Volume IX, N°. **97—108.**

## Erratum Communication N°. 101*a*.

p. 5 table I 2nd column: for — 102°.671 read — 103°.671.

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the wire. These values have been compared with formula $A_I$ of § 6 of Comm. N° 95*c*. The fifth column contains the deviations from this formula [1]. The sixth column contains the differences which were to be expected according to Comm. N°. 95*c*. The seventh column contains the differences between the two resistance thermometers in Ω.

TABLE I. Comparison of the platinum thermometer $Pt'_I$ with the hydrogen thermometer.

| Date 1907 | Temperature according to the hydrogen thermometer | Resistance in Ω | Resistance recalculated | $O_{Pt'_I} - C_{AI}$ | $O_{PtI} - C_{AI}$ | $O_{Pt'} - O_{Pt}$ |
|---|---|---|---|---|---|---|
| July 3 | — 102°.671 | 79.131 | 80.551 | — 0.000 | — 0.023 | + 0.023 |
| July 3 | — 119°.730 | 70.190 | 71.450 | + 0.003 | | |
| July 3 | — 164°.113 | 45.054 | 45.863 | + 0.047 | | |
| March 25 | — 182°.352 | 34.492 | 35.111 | — 0.008 | — 0.029 | + 0.021 |
| June 29 | — 216°.610 | 14.936 | 15.204 | + 0.016 | + 0.028 | — 0.012 |
| March 19 | — 252°.822 | 1.9208 | 1.9553 | + 2.4131 | + 2.432 | — 0.019 |
| July 1 | — 252°.839 | 1.9243 | 1.9588 | + 2.4180 | + 2.432 | — 0.014 |
| March 19 | — 255°.177 | 1.6852 | 1.7154 | + 2.0518 | | |
| July 1 | — 258°.864 | 1.4522 | 1.4783 | + 0.4855 | + 0.199 | + 0.287 |

## § 3. *Results.*

In order to be able to make conclusions from table I we remark that the later determinations have been made with the same thermometer filled with distilled hydrogen [2].

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[1] So $O_{Pt'I}$ is the resistance of the wire after its being broken and repaired $(Pt'_I)$ multiplied by 1.01806.

[2] With the earlier determinations this was the case for only some among them. We may derive from former measurements (comp. Comm. N°. 95*e*), that this will give no difference till — 217°, but for measurements in hydrogen this has not been proved experimentally. The method of filling by means of electrolytic hydrogen, provided it be done carefully, may be considered as perfectly satisfactory also for these temperatures. As this method, however, involves a more complicate system of auxiliary apparatus the other must be preferred with regard to the reliability.

From the results of table I and some earlier determinations at the same temperatures made with the resistance thermometer before it was broken, we may derive:

1. A comparison between the indication of the resistance thermometer before and after the breaking of the wire, abstracting from the reading errors of the hydrogen and resistance thermometers, by means of the determinations of March 25, June 29, and July 3. They give only small differences for the observations on the last two dates. Indeed if we compare the differences $O—C_{AI}$ of table II of Comm. N⁰. 95*c* with those of table I of this Communication, the differences for —103°, —183° and —217° ¹) respectively are:

$$+ 0.023, \ + 0.021 \text{ and } - 0.012$$

corresponding to

$$0^{\circ}.040, \ 0^{\circ}.036 \text{ and } 0^{\circ}.022.$$

From this we derive that down to — 217° the variations in the temperature coefficients owing to the new winding of the wire, though not imperceptible are extremely small.

2. A comparison between two resistance calibrations, for which the same hydrogen and resistance thermometers were used, in the neighbourhood of the boiling point of hydrogen by means of the determinations of March 19 and July 1. The difference is $0.0049\ \Omega = 0^{\circ}.046$ and exceeds $\frac{1}{50}$ deg. which has been derived as the limit of accuracy for measurements to —217°. This must

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¹) For —217° this difference just reaches the limit of accuracy derived in Comm N⁰. 95*e* and for the two other temperatures the difference only little exceeds this limit.

For —183° another reason may be given for this difference. To a certain extent it must probably be ascribed to the circumstance that the earlier determinations (of June 30 and July 6 '06) like those at —217° of June 30 '06 must be considered as less reliable. It appeared namely during an investigation started in Dec. 1906 that the steel capillary was no longer absolutely tight and this may also have been the case when the measurements under discussion were made. The latter becomes probable when we direct our attention to the great variations of the zero during these determinations, viz. 0.33 mm., to which we alluded in § 11 of Comm. N⁰. 95*e* without being able to explain it then.

The fault may have arisen because at the end of May '06 the thermometer has partly been taken to pieces and the capillary was bent too much. The observations made before June '06 were not influenced by this fault.

probably be ascribed to the fact that the measurements of the resistance are less accurate because they are made with the WHEATSTONE bridge and not with the differential galvanometer [1]).

3. A comparison between the indications of the thermometer filled with distilled hydrogen and the one used before and filled with electrolytical hydrogen, by means of the determination of July 1, abstracting from the errors of observation of the hydrogen and the resistance thermometers and variations in the temperature coefficients of the resistance [2]).

The difference appears to be larger than we should expect after the experience made with the higher temperatures. It may be that in the measurement of May 5, '06, the first measurement made in liquid hydrogen, in the measurement of the resistance or the reading of the hydrogen thermometer a systematic error has crept in, which escaped our attention. At any rate it will be necessary to repeat the calibration at these lowest temperatures.

The differences treated in this section, in so far as they go beyond the expected limit of accuracy, point partly to abnormal sources of error, partly to errors which in future may be prevented (as for instance by always measuring small resistances by means of the differential galvanometer) and it is probable that when we avail ourselves of the experience made we shall reach also for temperatures below — 217° an accuracy to 0°.02.

§ 4. In the same way as Comm N°. 95*e* § 7 the following observations, where two resistance thermometers were simultaneously immersed in the same bath, allow us to judge of the accuracy with which a temperature is fixed by a given resistance.

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[1]) The accuracy of the WHEATSTONE bridge is perfectly sufficient for higher temperatures below 0° C. (comp. Comm. N$^0$. 99*b* § 2 for temperatures till —217°), but owing to the disadvantageous influence of the connecting resistances, it falls short for measurements in hydrogen where the variation of the resistance becomes so small. Therefore, simultaneously with the measurements of table I in hydrogen made with the WHEATSTONE bridge, we have calibrated another thermometer $Pt_{d'}$ with the differential galvanometer, in order to fix the temperatures below —217°.

[2]) Although it is not excluded that here the variation of the temperature coefficients is larger than above — 217°, this can by no means explain the large deviation because the wire had previously been carefully annealed. Moreover it is difficult to assume that impurities of the gas in the thermometer would be the cause, for then we must accept that about 0.7% of air has been present in the gas, which is rather impossible on account of the great carefulness observed when the thermometer is filled.

With $Pt_I$ we have made an adjustment to a definite temperature at which the resistance of $Pt_{III}$ was determined, then the temperature was changed a little and again read on $Pt_I$ and then the resistance of $Pt_{III}$ was determined and reduced to the first temperature.

temp. on $Pt_I$ — 87°.54, resistance $Pt_{III}$ 103.950 Ω 1)
new „ „ „ reduced — 87°.54, „ „ 103.959 difference 0 009 Ω or 0°.014

temp. on $Pt_I$ — 216°.65 17.379
new „ „ „ reduced — 216°.65 17.385 difference 0.006 Ω or 0°.009

The probable error of an adjustment of the resistance thermometer appears to be equal to that of a reading on the hydrogen thermometer (comp. N⁰. 95*e* § 7) 2).

The following observations related to the defining of a temperature over a longer recording period.

$Pt_{III}$ and $Pt_V$ were calibrated immediately after each other with $Pt_I$, thence we derived the temperature reading according to $Pt_I$ on $Pt_{III}$ and $Pt_V$. Afterwards and adjusted to the same temperature we have compared the gold thermometer $Au_0$ with $Pt_{III}$ and $Pt_V$ immediately after each other. The readings were

| temp. $Pt_I$ on $Pt_{III}$, | temp. $Pt_I$ on $Pt_V$, | $Au_0$ resistance 3) |
|---|---|---|
| — 58°.56 | — 58°.56 | 40.324 |
| — 87°.43 | [— 87°.50] | 34.638 |
| —159°.07 | —159°.08 | 20.393 |
| —216°.27 | —216°.29 | 8.459 |

---

1) For small differences in the calibrations of $Pt_{III}$ and $Pt_V$ we refer to Comm. N⁰. 99*b* where also the zero's are given. The differences result from a more accurate determination of the ratio between the arms of the WHEATSTONE bridge and of the resistance of the conducting wires. In observations which were made from 1905—1907 it appeared that the zero's had remained unchanged to less than $\frac{1}{20000}$ (comp. also Comm. N⁰. 99*b*).

2) In Comm. N⁰. 95*e* § 7 we for the time being took as a starting point that the error in the adjustment of the hydrogen thermometer was negligible.

3) These values deviate a little from the values given in table III of Comm. N⁰. 95*d* owing to corrections which were afterwards determined.

If we disregard the large deviation in brackets which indicate that it must be ascribed to an irregularity, it appears that the definition of a temperature by means of a single determination on a resistance thermometer has about the same probable error as a single determination with the hydrogen thermometer and is generally reliable to an amount which remains below 0°.02.

For the present the accuracy of the determination of a temperature which is kept constant during a long time by means of the hydrogen thermometer may be considered equal to the accuracy of the definition of a temperature by means of the resistance thermometer, where however the necessary readings, even when they are repeated, require less time.

§ 5. According to § 3 the observations of June 30 and July 6, '06 must be rejected. They have been used for the calibration of the thermo-element and the resistance thermometer of Comms. N$^{os}$. 95*a*, 95*c* and 95*f* and hence the values — 217°.411 and —182°.75 of the tables VIII of Comm. N$^{0}$. 95*a*, I, II of Comm. N$^{0}$. 95*c* and IX of Comm. N$^{0}$. 94*f* must be modified.

The determination of June 30, '06 at — 183° shows a perceptible difference with that of March 25, '07, the only one of the required reliability. In observation 11 of table VIII we must therefore replace —182°.75 by —182°.79 and an analogous modification is required in the tables I, II and IX.

Instead of the values which relate to —182°.75 of table II we now get:

TABLE II. Values for — 183° instead of those of table II of Comm. N$^{0}$. 97*c*.

| $t$ | Number of observations | $O—C_{AI}$ | $O—C_{AII}$ | $O—C_{B}$ | $O—C_{C}$ |
|---|---|---|---|---|---|
| —182.79 | 2 | —0.008 | +0.048 | +0.104 | —0.014 |

The agreement is thereby greatly inproved, as $O—C_{AI}$ is changed from — 0.029 to — 0.008.

In the tables VIII of Comm. N$^{0}$. 95*a* and IX of Comm. N$^{0}$. 95*f* the three temperatures — 183° from which a mean has been derived, are all diminished by 0°.04. O—C thereby becomes less by 0.0008 and the agreement improves in the same rate.

As to the determination of July 6, '06 the modification is very small.

In the tables VIII of Comm. N°. 95*a* and IX of Comm. N°. 95*f* no change occurs if we omit this last determination in the mean, in tables I and II it is not used.

With regard to this and to what has been said in note 1 of § 13 of Comm. N°. 95*a*, no new calculation has been made.

As a supplement to columns 2 and 3 of table I towards a complete calibration of $Pt_I'$ we can use $Pt_I$ in table V of Comm. N° 99*b* with the zero 135.438 Ω (comp. note 1 of § 4).

**Erratum Communication N°. 101.**

p. 10 line 13 from the top: for „§ 4" read: „§ 2".

# COMMUNICATIONS

FROM THE

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AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

## No. 101b.

**Dr. H. KAMERLINGH ONNES and C. BRAAK.** "On the measurement of very low temperatures. XVIII. The determination of the absolute zero according to the hydrogen thermometer of constant volume and the reduction of the readings on the normal hydrogen thermometer to the absolute scale."

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam,* **30 November 1907**, p. 427—430).

EDUARD IJDO — PRINTER — LEIDEN.

## **Dr. H. KAMERLINGH ONNES and C. BRAAK.** "*On the measurement of very low temperatures.* XVIII. *The determination of the absolute zero according to the hydrogen thermometer of constant volume and the reduction of the readings on the normal hydrogen thermometer to the absolute scale.*"

### § 1. *The determination of the absolute zero.*

D. BERTHELOT [1]) has used the observations of CHAPPUIS on the pressure coefficients between 0° C. and 100° C. and the slopes of the $pv$-lines at 0° C. and 100° C. to derive the mean relative pressure coefficient from 0° C. to 100° C. which the investigated gas would possess for densities in the state of AVOGADRO (so we call for shortness the state in which the deviations from the law of BOYLE-GAY-LUSSAC-AVOGADRO may be neglected). In the same way we may use for this purpose the data of Comm N⁰. 100*b* and Comm N°. 60.

If for the pressure coefficient of the hydrogen thermometer for a zero pressure of 1090 mm. and a density of 1.44 as found in Comm. N⁰. 60 we take the value 0.0036627, we may derive the pressure coefficient for the state of AVOGADRO (represented by $\alpha_{AV}$) from the data of Comm. N⁰. 100*b* for $B_A$ for 0° C. and for 100.°20 C. by means of the formula:

$$100 \times 0.0036627 = \frac{A_{A0} \times 100\ \alpha_{AV} + (B_{A100} - B_{A0}) \dfrac{1090}{760}}{A_{A0} + B_{A0} \dfrac{1090}{760}}, \qquad (1)$$

where we must replace the value of $A_{A0}$ found in § 3 of Comm N°. 100*b* by a more accurate value:

$$A_{A0} = 1 - B_{A0} - C_{A0} = 0.999419$$

---

[1]) Sur les thermomètres à gaz. Travaux et Mémoires du Bureau international des Poids et des Mesures, t. 13.

and where $B_{A100}$ has been derived from $B_{A0}$ and $B_{A100.20}$ by interpolation [1]). Hence follows for the desired pressure coefficient

$$\alpha_{AV} = 0.0036617.$$

The reciprocal gives the temperature of the freezing point measured on the absolute scale. Hence:

$$T_{0^\circ\,C.} = 273^\circ.10\ K.$$

where K. (KELVIN) stands for degrees on the absolute scale of which 100 occur between the freezing point and the boiling point of water.

The data are not sufficiently accurate to allow us to determine the last decimal to less than unity [2]) [3]). The value found here agrees very well with that which may be derived from the most reliable data of other observers [4]).

The method followed here of deriving the pressure coefficient for infinitely small densities by means of determinations of isotherms at pressures between 25 and 50 atmospheres is preferable to using either the data of CHAPPUIS or those of AMAGAT. It is true that in the former case the coefficient $C$ may be neglected without error arising, but the small difference of pressure has a bad influence on the determination of $B$. On the contrary with higher pressures, such as with AMAGAT's determinations, the coefficients $C$ and the higher ones have too much influence to allow an accurate derivation of the value of $B$. In our determinations $C$ is of so small account that an error in the estimation of $C$ may be neglected for the determination of $B$ [1]).

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[1]) In formula (1) the curvature of the $pv$-lines is left out of account, which is permissible.

[2]) In discussing the isotherms we intend to refer to a small systematic difference between the isotherms of hydrogen at 20° C. according to Comm. N°. 70 (May 1901) and those at 0° C. and 100° C. of Comm. N°. 100*b*. It rather points at $T_{0^\circ\,C.} = 273^\circ.09$ K.

[3]) We intend to determine this value still more accurately with nitrogen and helium by means of determinations of isotherms at 0° C. and 100° C. and of pressure coefficients between 0° C. and 100° C. where we proceed according to Comm. N°. 60 (the determination of $H_2$ is also repeated), but as a higher degree of accuracy is wanted (designated by that now reached with the determinations of the isotherms) we now take a reservoir of 300 c.c.

[4]) Comp. for this the note 1 of p. 34, XIV Comm. N°. 97*b*.

While therefore the influence of errors in $C_A$ may be neglected we find on the other hand that the pressures are so large that an error in the pressure coefficient passes diminished to about $\frac{1}{25}$ into the value of $B_A$. Hence in this way we have obtained data at a rather large difference of pressure, from which $B_A$ may be derived unambiguously.

## § 2. *Reduction of the readings on the normal hydrogen thermometer to the absolute scale.*

By means of formula (3) of § 2 of Comm. N°. 97*b* and with the new values of $B'_T$ (comp. formula (2) of § 2 Comm. N°. 97*b*) which may be derived from the data of table XXII, we have determined anew the corrections of the readings of the hydrogen thermometer of constant volume to the absolute scale. For this we have started from the individual virial coefficients and not as in Comm. N°. 97*b* from a general temperature formula, because the course of the separate isotherms has now been ascertained sufficiently to render a similar previous adjustment superfluous.

For $B'_0$ and $B'_{100}$ we have adopted other values than in Comm. N°. 97*b*. We have namely used the results obtained from direct determinations of isotherms at 0° C. and 100° C., of which the results are laid down in Comm. N°. 100*b*. These values are:

$$B'_0 = 0.0005807 \quad , \quad B'_{100} = 0.0006321.$$

For the absolute zero we have adopted

$$t = -273^\circ.10 \text{ C.}$$

---

[1]) If for instance in the adoption of $C_A$ an error of 15 % has been made, which with a view to the data of table XXII of Comm. N°. 100*a* probably includes the higher limit for the error for lower temperatures, this becomes only 0.0000001 which, considering that the greatest density which occurs in the determinations of Comm. N°. 100*b* amounts to about 50 times the normal one, would cause for 0° C. an error in $B_A$ which remains below 0.000005. As such a systematic error would change the value of $C_{A.100^\circ}$ in nearly the same way, the error in this difference will be much smaller and, for instance, the error arising thence in the difference between $B_{A.0^\circ}$ and $B_{A.100^\circ}$ may be estimated at 0.000001, i. e. $1/5$ of the error in the absolute value of $B_A$. The error in the absolute zero arising from the two influences combined remains below 0°.01 C.

TABLE XXV. $H_2$. Corrections to the absolute scale.

| $t'_s$ | $\theta$ | $B'_T . 10^3$ | $\Delta t_s$ | $\Delta t$ | $(O-C)\times 10^3$ |
|---|---|---|---|---|---|
| — 103°.57 | — 103°.55 | + 0.394 | 0.017 | + 0.016 | 0 |
| — 139.88 | — 139.85 | + 0.229 | 0.029 | 0.026 | — 1 |
| — 164.14 | — 164.10 | + 0.018 | 0.043 | 0.039 | + 1 |
| — 182.81 | — 182.76 | — 0.241 | 0.056 | 0.051 | + 3 |
| — 195.27 | — 195.21 | — 0.432 | 0.059 | 0.054 | — 3 |
| — 204.70 | — 204.63 | — 0.692 | 0.069 | 0.063 | — 2 |
| — 212.82 | — 212.74 | — 1.009 | 0.079 | 0.072 | + 1 |
| — 217.41 | — 217.33 | — 1.203 | + 0.083 | + 0.076 | + 1 |

derived in the previous § from the same determinations of isotherms. The results have been combined in the preceding table in the manner of table XVI of Comm. N°. 97*b*.

The differences with the earlier values remain, notwithstanding we have used entirely different data, far within the limits of the accuracy mentioned in § 3 (loc. cit.). The coefficients of the formula given there become:

$$
\begin{aligned}
a &= -\,0.007117\\
b &= +\,0.005962\\
c &= -\,0.000185\\
d &= +\,0.001330
\end{aligned}
$$

With this formula the temperatures of the second column have been determined. The differences between the data of the last column but one and the formula are given in the last column.

For — 273° the new formula gives the same value as the one before of Comm. N°. 97*b* i.e. $\Delta t = +\,0^\circ.14$, for 0° C. and + 100° C. it gives $\Delta t = 0^\circ$. For the temperatures between 0° C. and 100° C.

the formula yields much larger negative values than those which Berthelot has derived with his equation of state (loc. cit. IX). For 20°, 50° and 80° are found:

According to Berthelot:

$\Delta t = -0°.00064, \quad -0°.00053$ and $-0°.00033$,

according to our formula:

$\Delta t = -0°.0012, \quad -0°.0020$ and $-0°.0014$.

According to the general equation of state of hydrogen derived previously (comp. § 1 Comm N°. 97*b*) these values would be respectively:

$-0°.0026 \quad , -0°.0047 \quad , -0°.0036.$

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

## No. 102$^a$.

**Dr. H. KAMERLINGH ONNES.** "Isotherms of monatomic gases and their binary mixtures. I. Isotherms of helium between + 100° C. and — 217° C."

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam*, **28 December 1907**, p. 495—501).

EDUARD IJDO — PRINTER — LEIDEN.

## **Dr. H. KAMERLINGH ONNES.** "*Isotherms of monatomic gases and their binary mixtures.* I. *Isotherms of helium between* + 100° *C. and* — 217° *C.*"

(Communicated in the meeting of November 30, 1907).

§ 1. On account of the important rôle, which VAN DER WAALS's theory plays in many chapters of thermodynamics, experimental data concerning the equation of state of a substance are of the greater value as the interaction of the molecules of this substance conforms the better to the hypotheses from which VAN DER WAALS started. The knowledge of the equation of state of the monatomic gases, whose molecules we must consider for the present as the simplest is of the greatest importance from this point of view.

In Comm. N$^0$. 69 (March 1901) on the isotherms of diatomic gases and their binary mixtures it was already remarked that the investigation of the net of isotherms of argon and of helium promised still more important results than the completion of the net of isotherms of the gases formerly called permanent, particularly of hydrogen, at low temperatures, on which subject my attention had been chiefly fixed since the establishment of the cryogenic laboratory (cf. Comm. N$^0$. 14, Dec. '94). But the difficulty of obtaining argon and helium in so pure a state and in such quantities as are required for the determination of isotherms, retarded the determination of the equation of state of helium and argon for a long time after Comm. N$^0$. 69.

The investigations on the isotherms of hydrogen are in progress, and yielded already results laid down in communications N$^{os}$. 78, 97*a*, 99*a*, 100*a*, which, I hope, will soon be followed by others. In the meantime, however, also the difficulty of obtaining pure helium has been quite, that of obtaining pure argon nearly overcome. The successful preparation of pure helium was chiefly due to the hydrogen circulation (Comm. N$^0$. 94*f*) yielding the required liquid hydrogen. So the first measurements from the series which will refer to the monatomic gases and their binary mixtures, can already be communicated.

They concern the isotherms of helium, which have now taken the place occupied by the isotherms of hydrogen before the hydrogen was liquefied. Among others the isotherms must lead to the calculation of the critical quantities for helium. From the determinations communicated now on the compressibility along different isotherms at densities which are comparatively small and differ only slightly, the critical temperature can already be calculated by approximation.

## § 2. *Survey of the determinations.*

This investigation comprises some six determinations of isotherms. The temperatures at which they were made, were kept constant and determined in the same way as in the determinations of isotherms for hydrogen published in preceding Communications N°. 97*a* (December 1906), N°. 99*a* (June 1907), N°. 100*a* (Nov. 1907)[1]. The readings of the hydrogen thermometer were reduced to the absolute scale by means of formula (4) of Comm. N°. 97*b* (Jan. 1907) with the new coefficients of § 2 of Comm. N°. 101*b*. The six temperatures thus reduced to which the isotherms refer are: + 100°.35, + 20°.00, 0°, —103°.57, —182°.75 and — 216°.56.

Besides the measurements at the two standard temperatures 0° C. and 100° C.[2] and those at low temperatures a determination was made at 20° C. to obtain data for the calculation of the quantity of gas in the stem of the piezometer and in the other parts, which remain at the ordinary temperature during the measurements.

For all these isotherms the densities, at which the pressure was observed, lie between almost the same limits which were set by the dimensions of the piezometer and by the manometer. The utmost limits of the density are 25 and 54 times the normal one. The piezometer and further auxiliary apparatus were perfectly the same as have served for the determinations of C. BRAAK and me (see Comm. N°. 100*b*) with hydrogen at 0° C. and 100° C. The satisfactory results obtained then, enhance at the same time the reliability of the measurements considered now.

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[1] The cryostat used was that of Comm. No. 94.

[2] The results at 0° C. and 100° C. are incompatible with those of RAMSAY and TRAVERS, which, indeed, show strange deviations.

§ 3. *Results for* $pv_{\mathrm{A}}$.

The subjoined table contains the results of the determinations. The first column gives the number of the observation, the second the temperature measured on the absolute scale, the third the pressure in atmospheres, the two following ones the product $pv_{\mathrm{A}}$, and the density $d_{\mathrm{A}}$, in which the volume of the gas $v_{\mathrm{A}}$ is expressed in the normal volume (that at 0° C. and 1 atmosphere) and the density $d_{\mathrm{A}}$ in the normal density (that at 0° C. and 1 atmosphere). (Compare the corresponding tables of the above mentioned determinations of isotherms of hydrogen).

The calculation of these results was made as follows:

First the points of the isotherm of 20° C. were calculated (cf. also § 8 of Comm. N⁰. 78), and the coefficients $A_{\mathrm{A}}$ and $B_{\mathrm{A}}$ of the curve

$$pv_{\mathrm{A}} = A_{\mathrm{A}} + \frac{B_{\mathrm{A}}}{v_{\mathrm{A}}} + \frac{C_{\mathrm{A}}}{v_{\mathrm{A}}^2} \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

were determined from the 3 points by theaid of the method of least squares. For $C_{\mathrm{A}}$ a definite value was assumed, the densities being too small for this coefficient to be determined with sufficient certainty. If we write VAN DER WAALS's equation with the second correction for the size of the molecules in the form:

$$pv = RT + \frac{RT\,b - a}{v} + \frac{5}{8}\,\frac{RTb^2}{v^2},$$

where $v$ is the volume of the gas under the pressure $p$ at the absolute temperature $T$, expressed in the theoretical normal volume (see Comm. N⁰. 71 § 3) and put the value of $A_{\mathrm{A}}$ at 0°, $A_{\mathrm{A}0} = 1$, which approximation is allowed for our purpose, we find (cf. Comm. N⁰. 71 § 3) for the value $C_{\mathrm{A}_T}$ of $C_{\mathrm{A}}$ at $T$

$$C_{\mathrm{A}_T} = {}^5/_8\, RT\, b^2, \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where $R = 0.0036617$. The value of $b$ was first estimated at 0.0005 (cf. note 1 to § 6 p. 23 of Comm. N⁰. 96*c* Jan. 1907), afterwards at 0.000432, see § 4. With the coefficients $A_{\mathrm{A}}$ and $B_{\mathrm{A}}$ obtained for 20° in this way, the reductions to 0° for the gas which is outside the reservoir at a temperature of 20° and for a small part at the tem-

TABLE I. He. Values of $pv_A$.

| N°. | $\theta$ | $p$ | $pv_A$. | $d_A$. |
|---|---|---|---|---|
| 1 | + 100°.35 | 42.574 | 1.38725 | 30.689 |
| 2 | | 54.459 | 1.39314 | 39.091 |
| 3 | | 66.590 | 1.39929 | 47.589 |
| 4 | + 20°.00 | 27.539 | 1.08664 | 25.343 |
| 5 | | 36.303 | 1.09028 | 33.297 |
| 6 | | 53.708 | 1.09918 | 48.862 |
| 7 | 0° | 26.634 | 1.01392 | 26.268 |
| 8 | | 38.565 | 1.01851 | 37.864 |
| 9 | | 50.240 | 1.02521 | 49.004 |
| 10 | — 103°.57 | 20.580 | 0.63135 | 32.597 |
| 11 | | 24.100 | 0.63296 | 38.075 |
| 12 | | 29.185 | 0.63597 | 45.891 |
| 13 | | 33.383 | 0.63845 | 52.288 |
| 14 | — 182.°75 | 13.751 | 0.33787 | 40.699 |
| 15 | | 16.019 | 0.33898 | 47.257 |
| 16 | | 18.189 | 0.34025 | 53.457 |
| 17 | — 216°.56 | 9.564 | 0.21132 | 45.259 |
| 18 | | 10.502 | 0.21171 | 49.606 |
| 19 | | 11.448 | 0.21219 | 53.951 |

perature of the room, were carried out in first approximation. With the three points which were thus found on the isotherm of 0°, the virial coefficients $A_A$ and $B_A$ were then calculated also for this temperature.

From this follows $A_{A0}$, the value of $pv_A$ for $d=0$, by means of the formula:

$$A_{A0} = 1 - B_{A0} - C_{A0}.$$

With the pressure coefficient for 0° C. for the state of AVOGADRO, 0.0036617 (cf. § 1 of Comm. N°. 101*b*) follows for 20°:

$$A_{A20^\circ} = A_{A0}\,(1 + 0.0036617 \times 20),$$

so that on the isotherm of 20° a fourth point is acquired, which renders the slope of the $pv_A$ - line a great deal more certain (cf. the conclusion of § 1 of Comm. N°. 101*b*). Then the calculation of $A_A$ and $B_A$ was repeated, and by the aid of these corrected coefficients the isotherm of 0° C. was again calculated, and this calculation by approximations was continued till it caused no longer any change. In this way we found for 20° C. (for $b = 0.000432$):

$$pv_{A20} = 1.07273 + 0.0005337\, d_{20} + 0.000000125\, d_{20}^2 \quad . \quad . \quad (3)$$

With this formula the corrections have been calculated for the determinations of isotherms. For the rest the latter were treated as in the preceding communications.

§ 4. *Individual virial coefficients.*

We may avail ourselves of the data of table I in order to derive the coefficients $A_A$ and $B_A$ by the aid of the method of least squares. $C_A$ was assumed according to formula (2) of the preceding §. For every isotherm $pv_{A,d=0}$ was calculated, and this value was added to the others as if it concerned a new observed point. This calculation was effected by the aid of the value $A_{A_0} = 0.99949$, which may be derived from the value for the coefficients $B_A$ and $C_A$ for 0° finally obtained in the calculation by approximations from the conclusion of the preceding §. Table II contains the virial coefficients and at the same time the differences between the given $pv_A$'s and the calculated ones. These differences are arranged according to the ascending densities. So the first column of differences refers to $pv_{A,d=0}$, the others to the data of table I in the above succession.

The calculation of the $B_A$'s is still uncertain, because for $C_A$ estimated values have been assumed. Determinations of $pv_A$ at greater densities, which will render an independent determination of $C_A$ possible, are in preparation.

That the estimations of $C_A$ are not too inaccurate, may be made probable as follows. For 100° follows from table II $B_{A\,100^\circ} = 0.000673$.

On the suppositions on which VAN DER WAALS's equation rests, the value of $b$ may be derived from the value for two temperatures of $B = RTb - a$ with $B = B_A\,(A_{A_0})$ and then $b = 0.000432$ is found, which does not differ much from the value 0.0005, which was first assumed by way of estimation on other grounds. Though the calculation followed here is very uncertain, yet the found value was preferred to the first estimated one, and for this reason the calculations which were first made with 0.0005, have been repeated with this new estimation. The differences of the results lie within the limit of errors of observation.

TABLE II. He. Individual virial coefficients.
Deviations of the $pv_A$ from the calculated ones.

| $\theta$ | $A_A$ | $10^3.B_A$ | $10^6.C_A$ | $10^5.(O-C)$ | | | | |
|---|---|---|---|---|---|---|---|---|
| +100°.35 | 1.36667 | +0.673 | +0.16 | +10 | −21 | −10 | +22 | |
| + 20°.00 | 1.07273 | +0.534 | +0.13 | − 3 | +31 | −36 | + 8 | |
| 0° | 0.99970 | +0.512 | +0.12 | −20 | +80 | −75 | +15 | |
| −103°.57 | 0.62036 | +0.337 | +0.07 | +11 | − 7 | −32 | 0 | +27 |
| −282°.75 | 0.33066 | +0.176 | +0.04 | 1 | − 1 | − 8 | + 8 | |
| −216°.56 | 0.20693 | +0.096 | +0.02 | 0 | + 1 | − 3 | + 3 | |

§ 5. *Determination of the critical temperature of helium.*

From the data of table II we may arrive at a first estimation concerning the critical temperature of helium, as it is found from determinations of isotherms within the now accessible region of temperatures.

Extrapolation proves that the BOYLE-point will lie in the neighbourhood of —250° C. For hydrogen —166° was found for this (cf. Comm. N°. 100*a*). If we assume 30° K. for the critical temperature of hydrogen, then follows from this for helium

$$T_{k\mathrm{He}} = 6^\circ\ \mathrm{K}.$$

If this value of $T_k$ is adopted, the region of temperature — 217°

to — 183° for helium corresponds with that of 0° to + 200° for hydrogen. By applying the law of the corresponding states to the slopes of the $pv_A$-lines for the two substances in the neighbourhood of these equivalent limits of temperature, we arrive at a slightly lower value of the critical temperature, viz.

$$T_{k\mathrm{He}} = 5°.3\ \mathrm{K}.$$

This value too I think I may still consider as a highest limit for the critical temperature of He, as it seems probable to me, that He with respect to $H_2$ will deviate from the law of the corresponding states in this sense that the critical temperature will be found lower than would follow from the application of this law to corresponding states for values of the reduced temperatures many times larger than 1.

Now there can only be question of a first estimation based on determinations of isotherms The determination of the isotherms of — 253° and — 259°, which is in progress, will, I hope, soon lead to a more reliable estimation.

In conclusion I gladly express my thanks to Mr. C. Braak for his assistance in this investigation.

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

## No. 102b.

**Dr. H. KAMERLINGH ONNES.** "On the measurement of very low temperatures. XIX. Derivation of the pressure coefficient of helium for the international helium thermometer and the reduction of the readings on the helium thermometer to the absolute scale."

*(Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam,* **28 December 1907**, p. 501—504).

EDUARD IJDO — PRINTER — LEIDEN.

## Addenda Communication N°. 102.

p. 13 line 10 from the bottom: add a note: „this value becomes 0.0036614, when $T_{0^\circ C.} = 273.09$."

p. 14 line 11 from the top: add a note: „this value becomes 0.0036617, when $T_{0^\circ C.} = 273.09$."

## **Dr. H. KAMERLINGH ONNES.** “*On the measurement of very low temperatures.* XIX. *Derivation of the pressure coefficient of helium for the international helium thermometer and the reduction of the readings on the helium thermometer to the absolute scale.*”

(Communicated in the meeting of November 30, 1907).

§ 1. *Pressure coefficients of helium.* As the absolute zero is known with sufficient accuracy — from the Leiden observations on hydrogen may be derived $T_{0^\circ \mathrm{C.}} = 273^\circ.10$ K., a value which as it agrees with other determinations, is probably not far from the true one — we may by means of the virial coefficients $B_{\mathrm{A}}$ for helium at 0° C. and 100° C., determined in the preceding communication (N⁰. 102*a*), derive the pressure coefficients of helium at different densities for this range of temperature. For the pressure coefficient of the *international helium thermometer* [1]), i. e. the mean relative pressure coefficient from 0° C. to 100° C. for helium with the density belonging to the zero pressure of 1000 m.m. $\left[\overset{0^\circ \mathrm{C.}-100^\circ \mathrm{C.}}{\alpha_v}\right]_i$ or for shortness ${}_i\alpha_v$, the formula

$$100 \cdot {}_i\alpha_v = \frac{A_{\mathrm{A}0} \times 0.36617 + (B_{\mathrm{A},100^\circ \mathrm{C.}} - B_{\mathrm{A},0^\circ \mathrm{C.}}) \dfrac{100}{76}}{A_{\mathrm{A}0} + B_{\mathrm{A},0^\circ \mathrm{C.}} \dfrac{100}{76}} \quad . \; . \; . \quad (1)$$

yields

$${}^{\mathrm{He}}_{i}\alpha_v = 0.0036613.$$

If one considers that according to table II of Comm. N⁰. 102*a* the isotherm of 0° gives rather large values for O—C, then it seems that the isotherm of 20° C., where the O—C are only small, is more reliable for the derivation given above. Therefore I have calculated $\left[ \overset{0^\circ \mathrm{C.}-100^\circ \mathrm{C.}}{\alpha_v} \right]_{1000 \text{ m.m.}}$ by means of the data for 20° C. and 100°.35 C. With neglection of the deviations from the absolute scale for the hydrogen thermometer at 20° C., $B_{\mathrm{A}.0^\circ \mathrm{C.}}$ was determined by means of rectilinear extrapolation. This gave

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[1]) The scale of the hydrogen thermometer of constant volume at 1000 m.m. zero pressure is generally called the scale of the normal hydrogen thermometer (this was also done in Comm. N⁰. 97*b*). As 0° C. and 760 m.m. are accepted as the normal state for gases, it seems to me preferable to call the scale just mentioned the scale of the *international* hydrogen thermometer. In the same way we must speak of the international helium thermometer.

$$B_{\mathrm{A}.0^\circ \mathrm{C.}} = 0.0_3499,$$

whence

$$A_{\mathrm{A}0} = 0.99950.$$

With these new data we derive from formula (1) of this section

$$^{\mathrm{He}}_{i}\alpha_v = 0.0036616.$$

From the data for $B_{\mathrm{A}}$ of table II of the preceding Comm. and $T_{0^\circ \mathrm{C.}} = 273^\circ.10$ K. we may determine in the way mentioned in § 2 of Comm. N$^0$. 97*b* the corrections of the readings of the helium thermometer of constant volume with a given zero pressure to the absolute scale. They have been calculated for a zero pressure of 1000 m.m. and are combined in table I where the remaining columns have the same signification as the corresponding ones of table XVI of Comm. N$^0$. 97*b*.

TABLE I. Correction of the international helium thermometer to the absolute scale

| $\theta$ | $10^3 . B_T$ | $(\Delta t)_a$ | $(\Delta t)_b$ |
|---|---|---|---|
| 100°.00 | + 0.492 | | |
| 0° (*a*) | + 0.513 | | |
| 0° (*b*) | + 0.500 | | |
| — 103°.57 | + 0.544 | + 0°.0034 | — 0°.006 |
| — 182°.75 | + 0.532 | + 0.0158 | + 0 .002 |
| — 216°.56 | + 0.463 | + 0.0252 | + 0 .010 |

The corrections indicated with (*a*) are derived by means of the values of $B_{\mathrm{A}.0^\circ \mathrm{C.}}$ from the direct determination, for (*b*) we have used the value which is recalculated with $B_{\mathrm{A},20^\circ}$ (comp. the prece-

## Errata Communication N$^0$. 102*b*.

(already published in Suppl. N$^0$. 34*a* p. 17, note 3).

p. 14 table I: for $B_T$ read $B'_T$.

p. 15 line 22 and line 6 from the bottom, and p. 16 line 3 from the top: the indices $_{\mathrm{H}_2}$ and $_{\mathrm{He}}$ have been interchanged by error of print, read $t_{\mathrm{He}}-t_{\mathrm{H}_2}$, and $\theta_{\mathrm{He}}-\theta_{\mathrm{H}_2}$ respectively.

p. 16 line 13 from the top: for 0.0000009 read 0.0000014.
line 14 from the top: for 0.0036613 read 0.0036612.

ding Comm.). It is probable that on account of what has been said in the preceding section those of column (*b*) are the most reliable.

§ 3. *Determinations of other observers.*

For a comparison with the results of the two preceding sections we can only use the determinations of TRAVERS, SENTER and JAQUEROD. [1]) They have found:

1st. for the pressure coefficient of the helium thermometer at 700 m.m. zero pressure $\left[\begin{matrix}0^\circ\,C-100^\circ\,C\\ \alpha_v\end{matrix}\right]_{700}=0.00366255$ which agrees with 0.0036628 for $\left[\begin{matrix}0^\circ\,C-100^\circ\,C\\ \alpha_v\end{matrix}\right]_i$ and

2nd. for the difference between the indications of the helium thermometer $t_{He}$ and the hydrogen thermometer $t_{H_2}$ (each of about 1000 m.m. zero pressure) at the boiling point of oxygen $(t_{H_2}-t_{He})_{-180^\circ\,C.}=0^\circ.10$ and at that of hydrogen $(t_{H_2}-t_{He})_{-252^\circ\,C.}=0^\circ.20$, which differences are so considerable that CALLENDAR [2]) concludes thence that the corrections of the helium thermometer to the absolute scale are negative.

The two results which strongly deviate from mine may be readily explained if one adopts that the determination of the pressure coefficient of helium by TRAVERS, SENTER and JAQUEROD has not yielded the true value. For if the differences in indication found by them between their helium- and their hydrogen thermometers are reduced by means of the corrections of each of these thermometers to the absolute scale which are given in Comm. N°. 100*a* and in Table I of this Comm., to the difference in readings on the absolute scale, which are found at the same temperature by means of the hydrogen thermometer which gives $\theta_{H_2}$ and by means of the helium thermometer which gives $\theta_{He}$, there remains at — 182° a difference

$$(\theta_{H_2}-\theta_{He})_{-182^\circ}=0^\circ.10-0^\circ.049+0^\circ.002=0^\circ.05,$$

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[1]) Phil. Trans. Ser. A. Vol. 200, p. 105—180. KUENEN and RANDALL (Proc. Roy. Soc. Vol. 59) have made a determination, which, being only intended to show whether the helium behaved normally, is not made to the high degree of accuracy which is required for a comparison with isothermal determinations.

[2]) Phil. Mag. (6) 5, 1903.

whereas by extrapolation of the corrections found down to — 217° for — 252° one would find

$$(\theta_{H_2} - \theta_{He})_{-252°} = 0°.20 - 0°.12 + 0°.02 = 0°.10.$$

When calculating the temperatures $t_{iH_2}$ and $t_{iHe}$ the investigators mentioned have taken the pressure coefficient of the helium thermometer $\left( {}^{He}_{i}\alpha_v \right)_{\text{TRAVERS}}$ to be equal to that of the hydrogen thermometer at the same zero pressure (for 1000 m.m. therefore 0.0036626 according to our value of Comm. N°. 60). If the corrections applied by me are right that pressure coefficient must therefore, in order that at—182° $\theta_{H_2} - \theta_{He} = 0$, be diminished by 0 0000010 so that

$${}^{He}_{i}\alpha_v = 0.0036616$$

and in order that $\theta_{H_2} - \theta_{He} = 0$ at — 252° by 0.0000009 so that

$${}^{He}_{i}\alpha_v = 0.0036613.$$

The first value which has been derived without extrapolation and which is therefore the most reliable, appears to agree perfectly with the one derived by me from the isothermals in § 1.

With regard to the method of derivation followed here we may remark that it allows of a fairly large accuracy. Though the certainty of the determinations of temperature on which it is based may be doubted as far as regards the absolute value, yet the only difference which comes into account here is known with sufficient certainty. The calculation mentioned above therefore not only gives an explanation of the too large differences found by TRAVERS, SENTER and JAQUEROD, but is also a welcome control for the pressure coefficient of helium found in section 1.

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

## No. 102c.

**Dr. H. KAMERLINGH ONNES.** "Isotherms of monatomic gases and their binary mixtures. II. Isotherms of helium at — 253° C. and — 259° C."

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam,* 28 **Maart 1908**, p. 741—742.)

EDUARD IJDO — PRINTER — LEIDEN.

## **Dr. H. KAMERLINGH ONNES.** "*Isotherms of monatomic gases and their binary mixtures.* II. *Isotherms of helium at* — 253° C. *and* — 259° C."

(Communicated in the meeting of February 29, 1908).

§ 1. *Survey of the determinations.* The measurements were made in the same way as those of Comm. No. 102*a* (Dec. '07). The whole of the piezometer had a four times larger content, viz. about 2 liters, the piezometer reservoir on the other hand was more than four times smaller, it was, namely, somewhat more than 2 $cm^3$. Accordingly the densities to which the measurements refer, are considerably larger, and lie between 591 and 794 times the normal one. The temperatures at which the determinations were made, are, measured on the hydrogen thermometer of Comm. N$^0$. 95*e*,

$$t = -252°.84 \text{ C. and } t = -258°.94 \text{ C.},$$

from which by extrapolation by means of table XXV of Comm. N$^0$. 101*b* (Dec. '07), cf. § 3 of Comm. N$^0$. 102*b*, follows for the temperatures below 0° C. measured on the absolute scale

$$\theta = -252°.84 + 0°.12 = -252°.72$$
$$\text{and } \theta = -258°.94 + 0°.12 = -258°.82$$

The determination of the mean temperature of the gas in the capillary stem of the piezometer reservoir, with regard to the part that extends above the bath in the cryostate, required here greater accuracy than before, because compared with the quantity of the gas in the smaller reservoir that in the stem was of more importance. With a view to the determination of this mean temperature a cylindric reservoir of the same height as the capillary was placed by the side of and on a level with the capillary, which reservoir was filled with helium, and provided with an appliance to read the pressure in it ¹). By means of this pressure it is

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¹) A similar contrivance has been applied by different observers in the determination of the mean temperature of the capillary of a gas thermometer (TRAVERS, SENTER and JAQUEROD, Phil. Trans. A 200 (1902) p. 143).

easy to derive with the required accuracy what mean density for the gas in the capillary of the piezometer must be taken. At 0° the pressure in this auxiliary apparatus was 118.3 cm. of mercury. With the measurement at — 253° C. it varied between 33.1 and 51.1 cm., at — 259° C. between 31.8 and 48.1 cm.

§ 2. *Results for* $pv_A$.

The subjoined table contains the results of the determinations in the same way as table I of Comm. N$^0$. 102*a*.

TABLE I. Helium. Values of $pv_A$.

| N$^0$ | $\theta$ | $p$ | $pv_A$ | $d_A$ |
|---|---|---|---|---|
| 1 | — 252°.72 | 53.948 | 0.09120 | 591.53 |
| 2 | | 60.716 | 0.09533 | 636.92 |
| 3 | | 65.997 | 0.09867 | 668.87 |
| 4 | — 258°.82 | 40.012 | 0.06150 | 650.65 |
| 5 | | 46.222 | 0.06559 | 704.71 |
| 6 | | 53.326 | 0.07063 | 754.97 |
| 7 | | 52.797 | 0.07531 | 794.00 |

The corresponding values for $pv_{A,d=0}$ are:

| | |
|---|---|
| for — 252°.72 | $pv_A = 0.07455$ |
| for — 258°.82 | $pv_A = 0.05222$ |

§ 3. *Further results.* The number of points on every isotherm is too small, and the densities are too large to allow already now the derivation of the first individual virial coefficients of the polynomial of state (cf. § 4 of Comm. N$^0$. 102*a*). If, however, we make a graphical representation, it shows that the isotherm $pv_A$ for — 259° must exhibit a minimum and hence $B_A$ must be negative at this temperature. Further follows from the isotherm of $-253°$, that the intersection of this line with the axis $d = 0$ lies near the BOYLE-point Probably $B_A$ is also already negative at $-253°$ though only slightly. All this agrees very well with what was derived in § 5 of Comm. N⁰. 102*a*, and speaks for the validity of the extrapolation applied there with a view to the calculation of the critical temperature of the helium.

In conclusion I gladly express my thanks to Mr. C. BRAAK for his assistance in this investigation.

**Dr. H. KAMERLINGH ONNES and C. BRAAK.** "*On the measurement of very low temperatures. XX. Influence of the deviations from the law of* BOYLE-CHARLES *on the temperature measured on the scale of the gas-thermometer of constant volume according to observations with this apparatus*".

(Communicated in the meeting of February 29, 1908).

§ 1. In Comm. N⁰. 97*b* (Jan. '07) under XV the formula of CHAPPUIS (see Comm. N⁰. 95*e* (Oct. '06) form. (3)) for the calculation of the temperatures according to the hydrogen thermometer of constant volume was compared with formula (6) of XIV of the same Communication, in which formula attention has been paid to the deviations from the law of BOYLE, whereas they are neglected in CHAPPUIS' formula. As the result of this comparison we stated there that for a dead space of $^1/_{100}$ the mean relative pressure coefficient between 0° and 100° is to be increased with 2 units of the 7th decimal, and the pressure coefficient of the hydrogen thermometer at 1090 mm. zero point pressure was, therefore, to be put at 0.0036629 instead of at 0.0036627, a modification which is, however, so slight, that it just coincides with the limit of the errors of observation. We have just found out that for this calculation inaccurate values of $B^{(p)}_{0°}$ and $B^{(p)}_{100°}$ have been used. New calculations have revealed that the difference is much smaller than was stated just now, so that it is to be taken into account only for much higher values of the dead space and, with the exception of carbonic acid, has no influence even on CHAPPUIS' last decimal (the 8th). That the use of the incorrect $B^{(p)}$ was not detected, was due to the fact that the calculation of neglections indicated in XV had accidentally led to the same result, here, however, because the four corrections, as has been mentioned in XV, had been erroneously taken with the same sign, whereas they almost entirely cancel each other. We shall therefore in future keep to the unchanged pressure coefficient 0.0036627.

A consequence of the improved calculation is also that table

XVIII of Comm. N⁰. 97*b* can be dispensed with. The first two corrections derived in XV § 3 of the Communication mentioned, now become so small that they fall outside the region of observation. The correction calculated at the end of § 2 becomes somewhat smaller for CHAPPUIS' carbonic acid thermometer than has been given there, viz. $-0.22 \times 10^{-6}$, to which another correction of $-0.8 \times 10^{-7}$ is to be added, if also the expansion of the glass by the pressure of the gas is to be taken into consideration.

§ 2. The restoration of our former value 0.0036627 further involves the following modifications, which are of no importance as they do not exceed the errors of observation, but should be applied to make the agreement in the calculations complete:

1. that in table XVI of Comm. N⁰. 97*b* in the first column the values of table XII are restored, and so all the numbers in the last decimal are increased by a unit. The latter holds also for the values of the second column of table XVI.

2. that in table XVII of the same Communication the values of the first column, except the last two, are increased by a unit in the last decimal.

3. that no further corrections are required for the temperatures in table XVI of Comm. N⁰. 99*a* (see conclusion of § 14 of Comm. N⁰. 99*a*).

In translating Comms. Nos. 100, 101 and 102*a*, *b*, as well as in *c*, the corrections required by this circumstance have already been taken into account.

# COMMUNICATIONS
FROM THE
# PHYSICAL LABORATORY
AT THE
# UNIVERSITY OF LEIDEN
BY
PROF. DR. H. KAMERLINGH ONNES,
*Director of the Laboratory.*

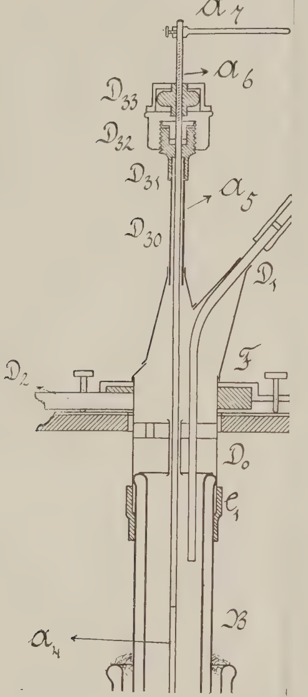
## No. 103.

**JEAN BECQUEREL and H. KAMERLINGH ONNES.** "The absorption spectra of the compounds of the rare earths at the temperatures obtainable with liquid hydrogen, and their change by the magnetic field." (*With five plates*).

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam,* **29 Februari 1908**, p. 678—690.

EDUARD IJDO — PRINTER — LEIDEN.

**JEAN BECQUEREL and H. KAMERI**
**compounds of the rare earths**
**and their change by the magneti**



**JEAN BECQUEREL and H. KAMERLINGH ONNES.** "On the absorptionspectra of the compounds of the rare earths at the temperatures obtainable by liquid hydrogen and their change by the magnetic field."

Pl. I.

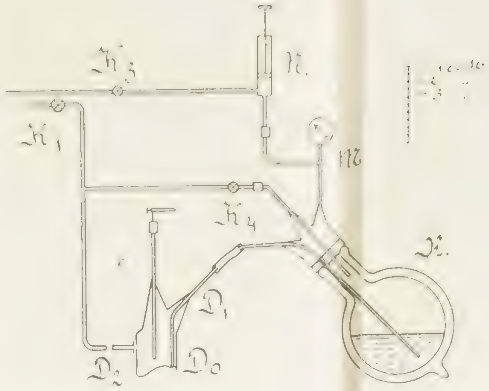


Fig. 4.

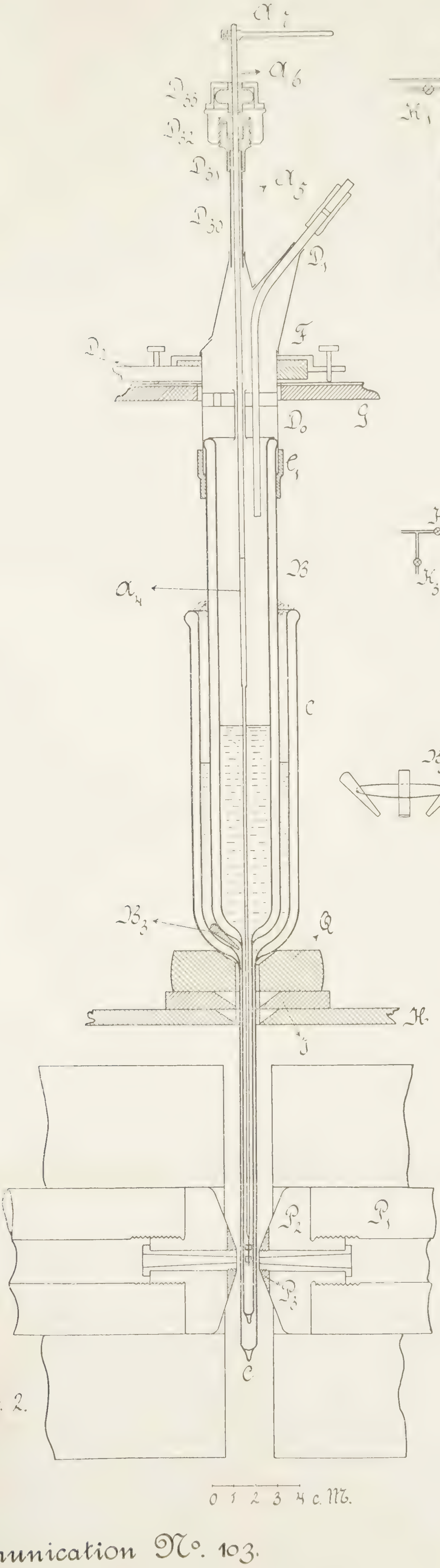


Fig. 2.

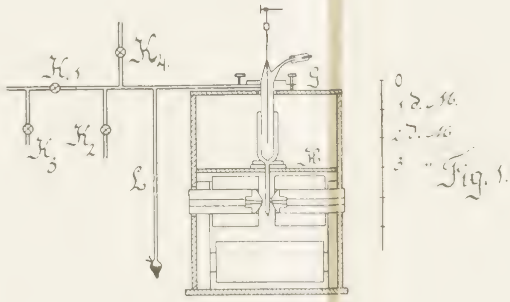


Fig. 1.

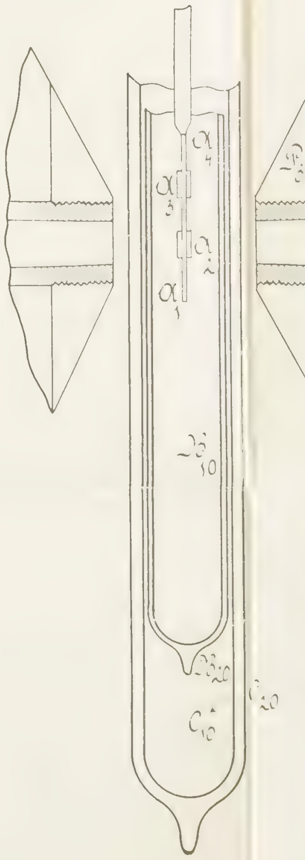


Fig. 3.a.

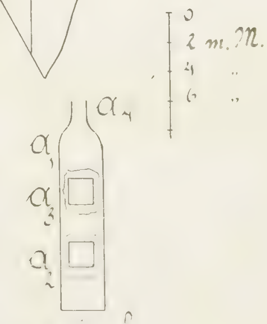


Fig 3. b.

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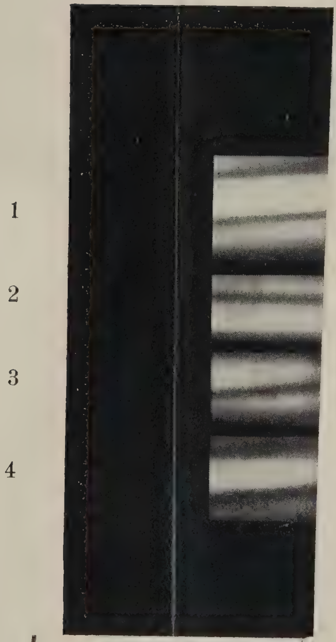
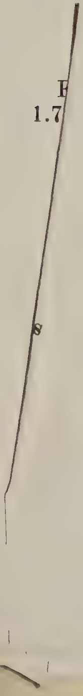
**JEAN BECQUEREL and H.**
**rare earths at the temper**





**JEAN BECQUEREL** and **H. KAMERLINGH ONNES**. "On the absorptionspectra of the compounds of the rare earths at the temperatures obtainable by liquid hydrogen and their change by the magnetic field."

Pl. II.

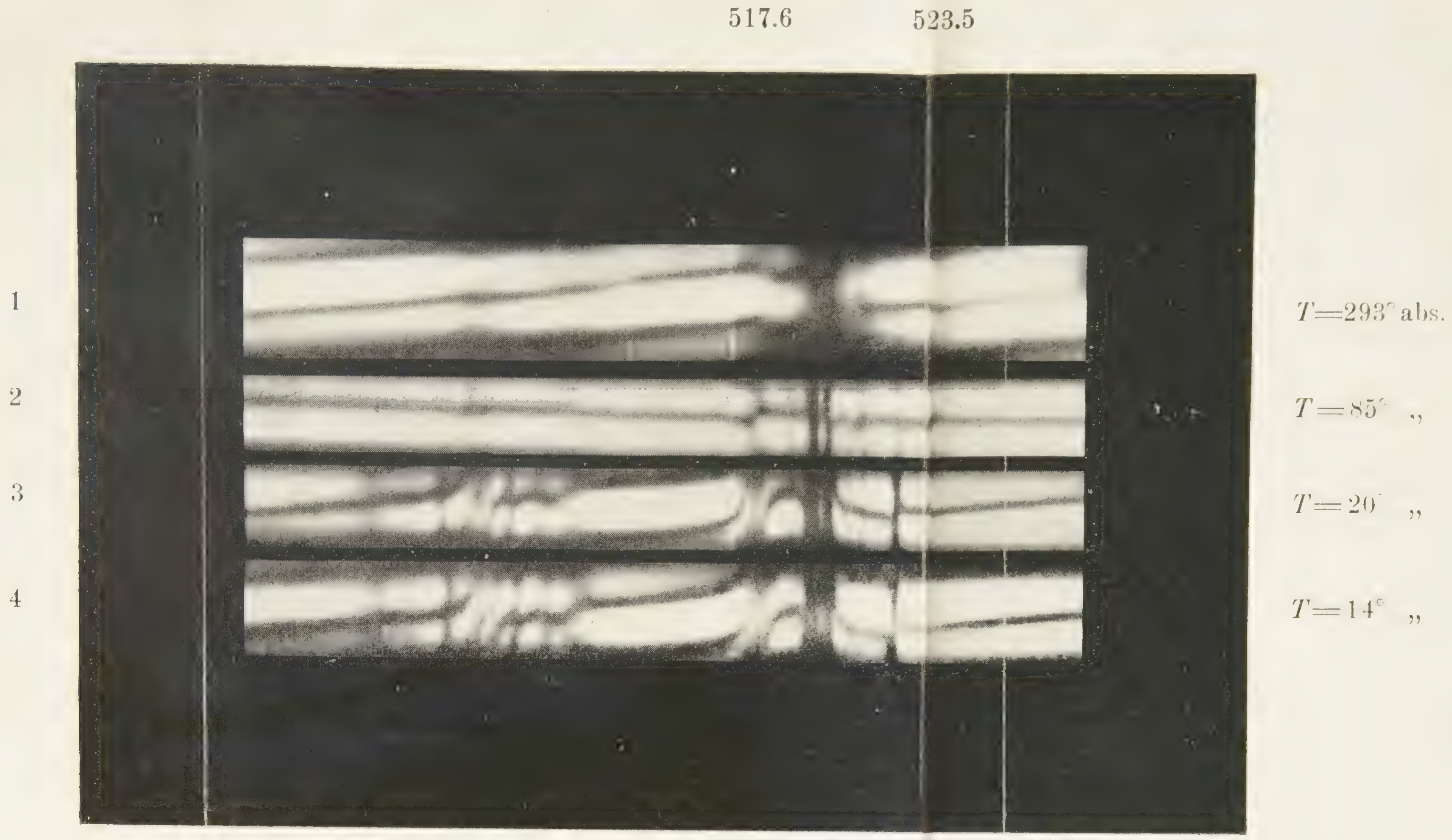


Fig. 1. *Anomalous birefrigency*, tysonite, group in the green 2d spectrum (Rowland grating), thickness of plates 1.71 mM. in 1, 3, 4 and 0.41 mM. in 2 (in 2 the ordinary and extraordinary ray are interchanged).

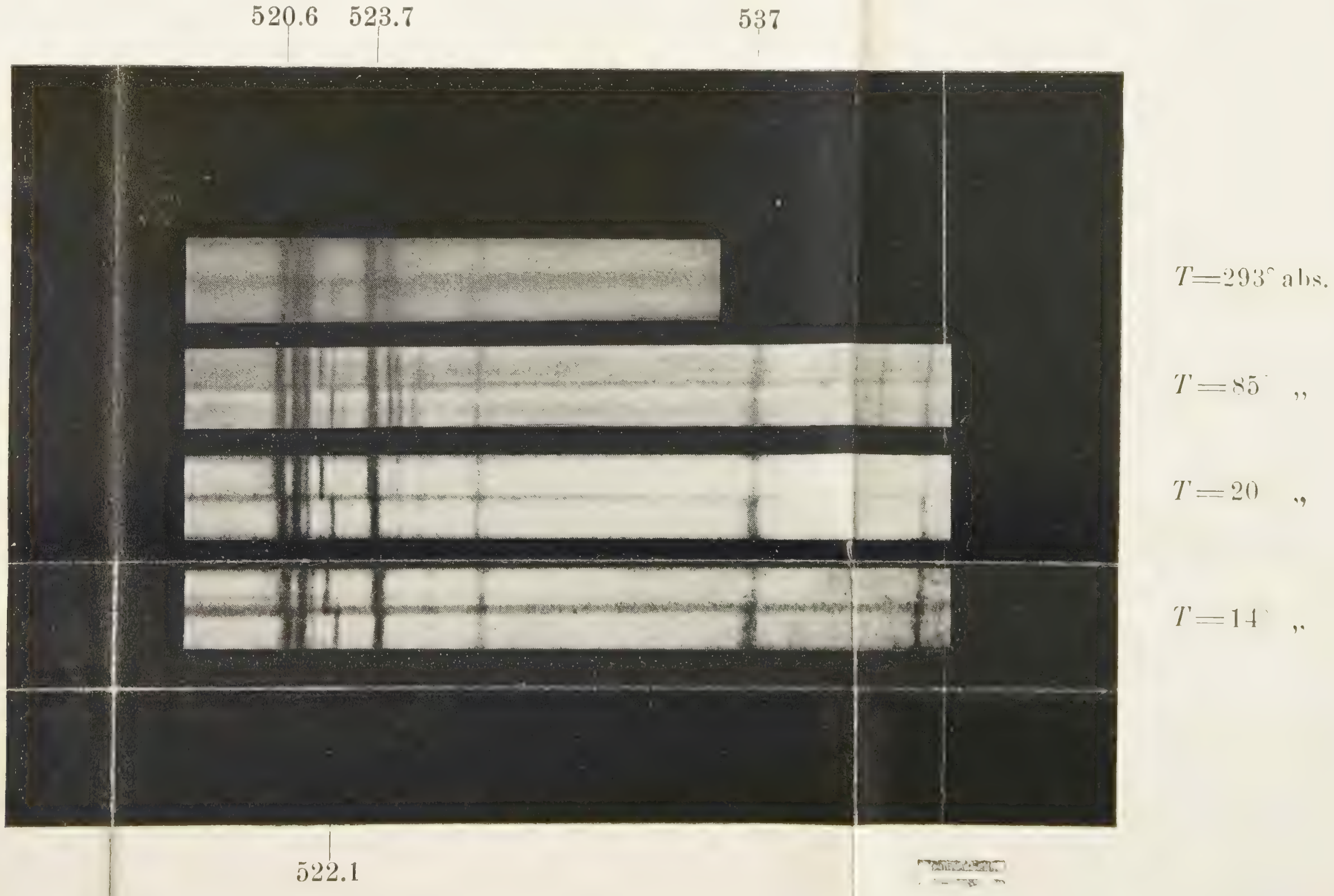


Fig. 2. *Left- and righthanded vibrations* in a field of about 18000 Gauss. Xenotime, group in the green, 2d spectrum (Rowland grating).

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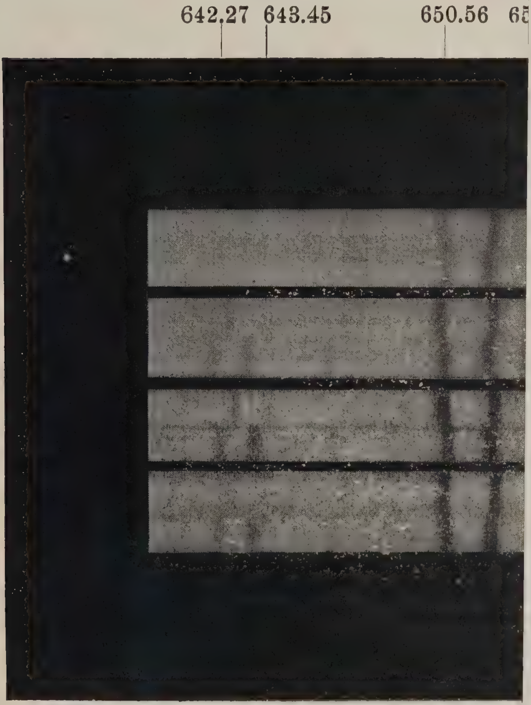
**JEAN BECQUEREL and H. KAMERLINGH ON**
**compounds of the rare earths at the temp**
**and their change by the magnetic field.”**



**JEAN BECQUEREL and H. KAMERLINGH ONNES. "On the absorptionspectra of the compounds of the rare earths at the temperatures obtainable by liquid hydrogen and their change by the magnetic field."**

**Pl. III.**

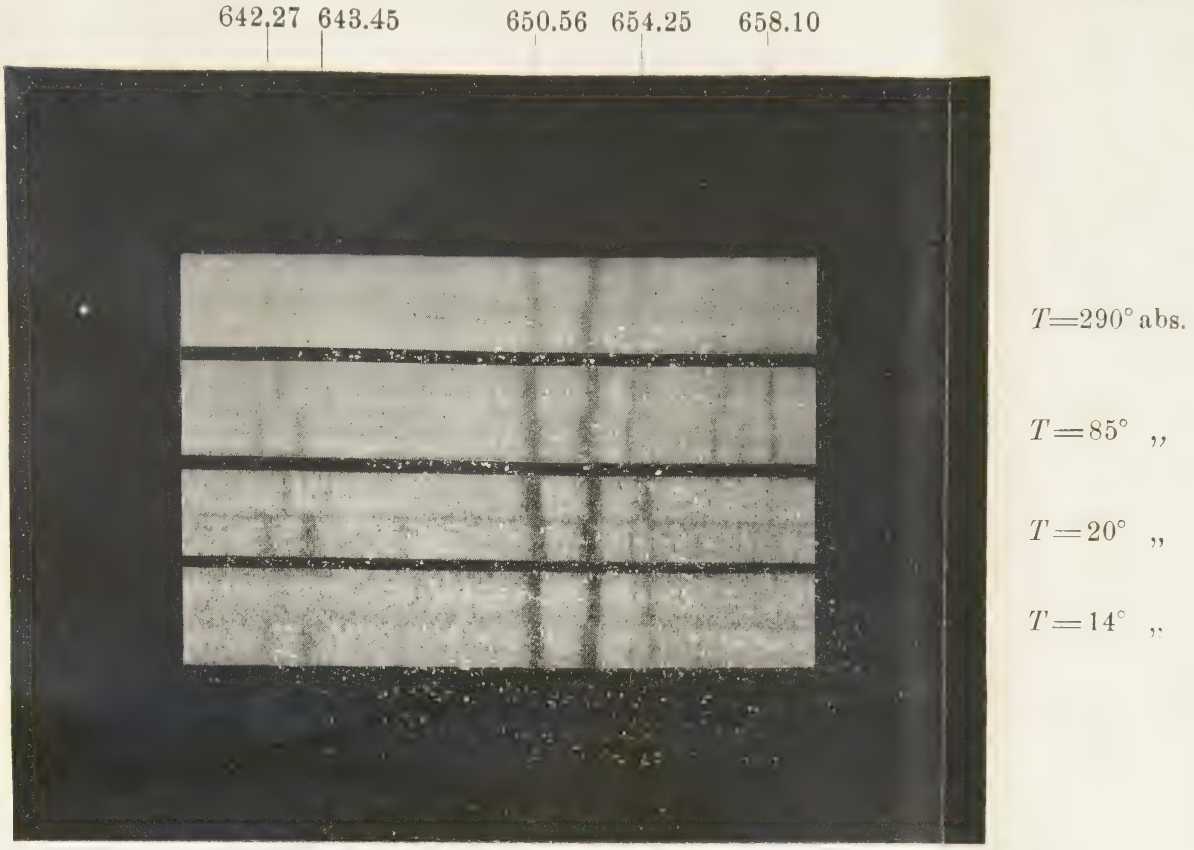


Fig. 3. *Left and righthanded vibration* in a field of about 18000 Gauss. Xenotime, group in the red, 2^d spectrum (Rowland grating); panchromatic plates of Wratten and Wainwright.

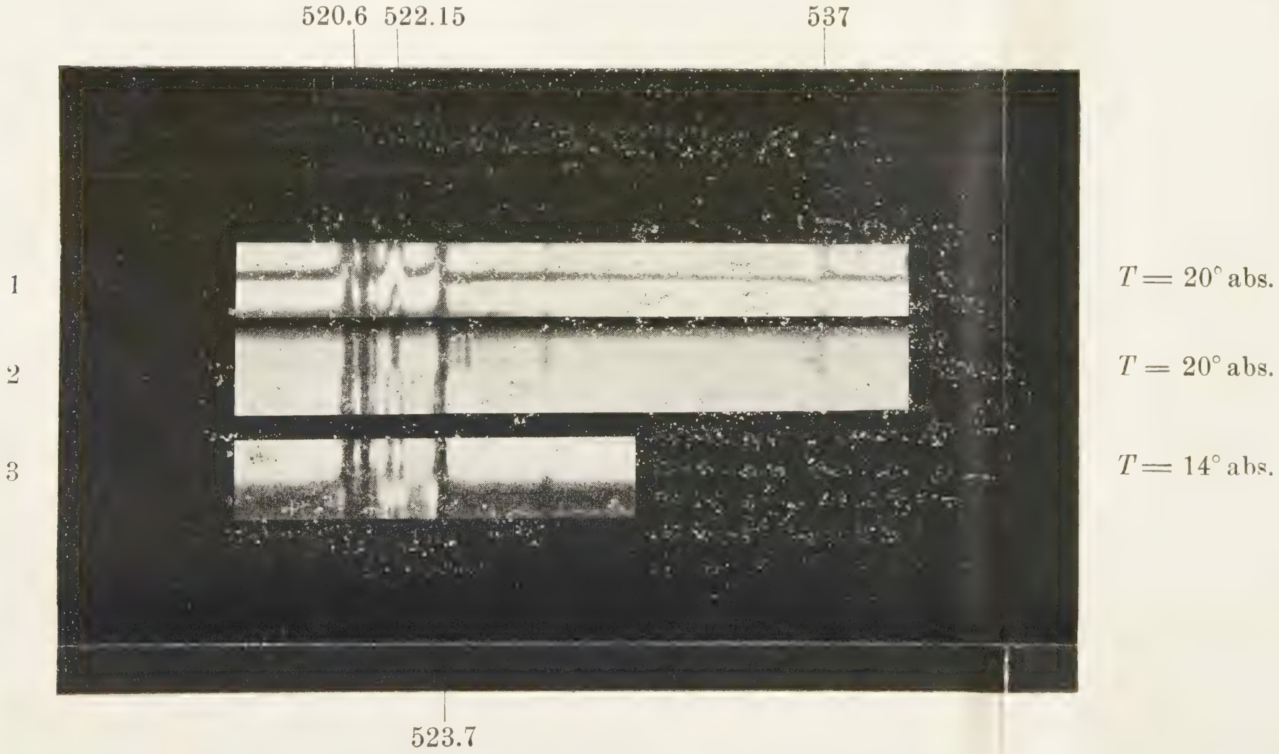


Fig. 4. *Xenotime,* group in the green, 2^d spectrum (Rowland grating).

1. magnetic circular birefringency, plate thick 0.80 mM., field 15000 Gauss.

2. images by rhombohedron before slit, the incident light polarized to give equal intensities to the regions in the transparent part in the middle of the group. Field 15000 Gauss.

3. images given by rhombohedron before slit, incident light polarized under 45° with the horizon; field 18000 Gauss.

Communication N°. 103.

**JEAN BECQUEREL and H. KAME**
**compounds of the rare earths**
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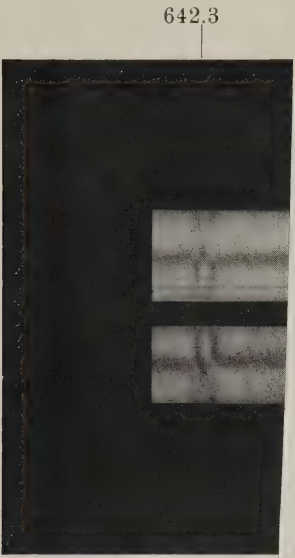

Fig. 5. *Magnetic rotation*
(Rowland grating); thicknes
plate turned 90° in the one

**JEAN BECQUEREL** and **H. KAMERLINGH ONNES.** "On the absorptionspectra of the compounds of the rare earths at the temperatures obtainable by liquid hydrogen and their change by the magnetic field."

**Pl. IV.**

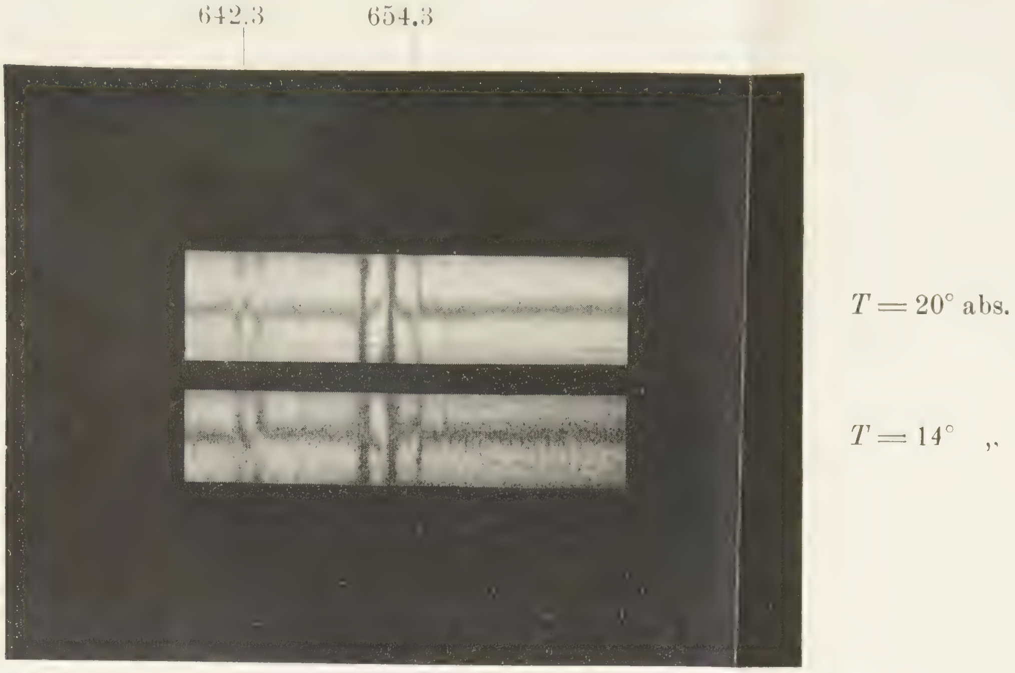

Fig. 5. *Magnetic rotation of the plane of polarization.* Xenotime 2ᵈ spectrum (Rowland grating); thickness 0.80 mM., field 18000 Gauss; (quarter of wavelength plate turned 90° in the one in respect to the other).

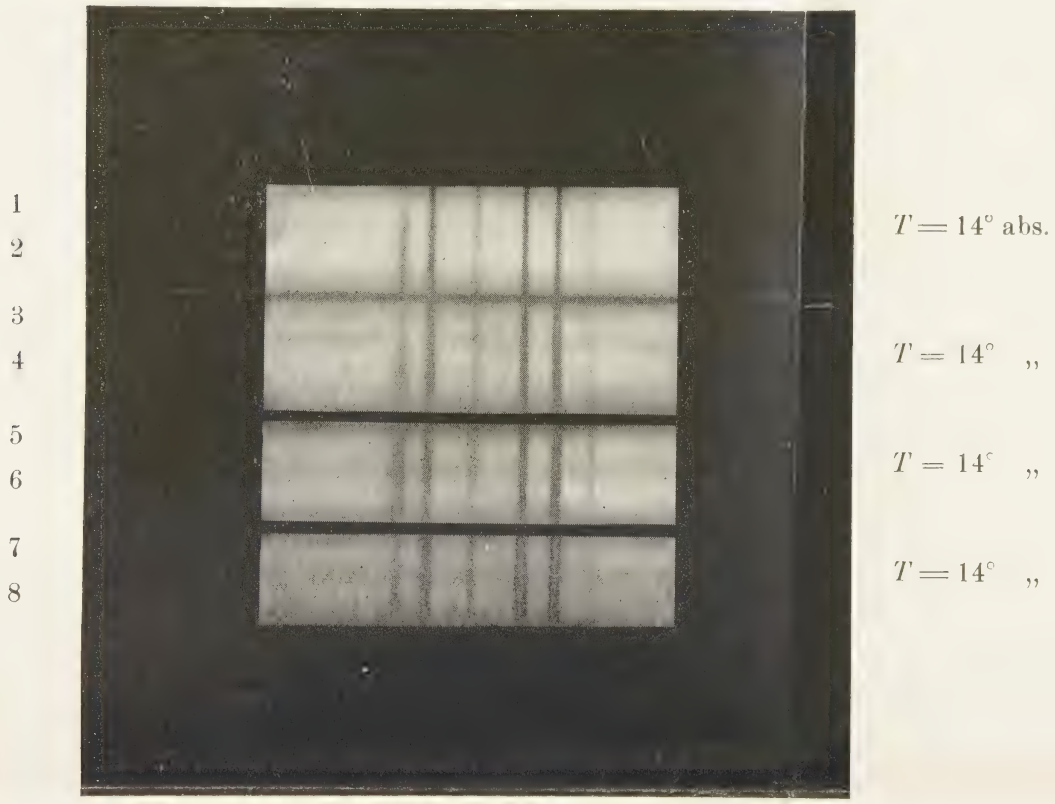

Fig. 6. *Sulphate of Neodyme,* group in the orange, 2ᵈ spectrum (Rowland grating) spectra of the vibrations:

1 in the principal direction *a*, field = 0.
2 ,, ,, ,, ,, *b*, field = 0.
3 ,, ,, ,, ,, *a*, *a* and *b* normal to the field (18000 Gauss).
4 ,, ,, ,, ,, *b*, *a* and *b* ,, ,, ,, ,, ,,
5 ,, ,, ,, ,, *a*, *a* and *c* ,, ,, ,, ,, ,,
6 ,, ,, ,, ,, *c*, *a* and *c* ,, ,, ,, ,, ,,
7 ,, ,, ,, ,, *b*, *b* and *c* ,, ,, ,, ,, ,,
8 ,, ,, ,, ,, *c*, *b* and *c* ,, ,, ,, ,, ,,

Communication N°. 103.

**JEAN BECQUEREL and H.**
**rare earths at the temper**

**JEAN BECQUEREL** and **H. KAMERLINGH ONNES.** "On the absorptionspectra of the compounds of the rare earths at the temperatures obtainable by liquid hydrogen and their change by the magnetic field."

**Pl. V.**

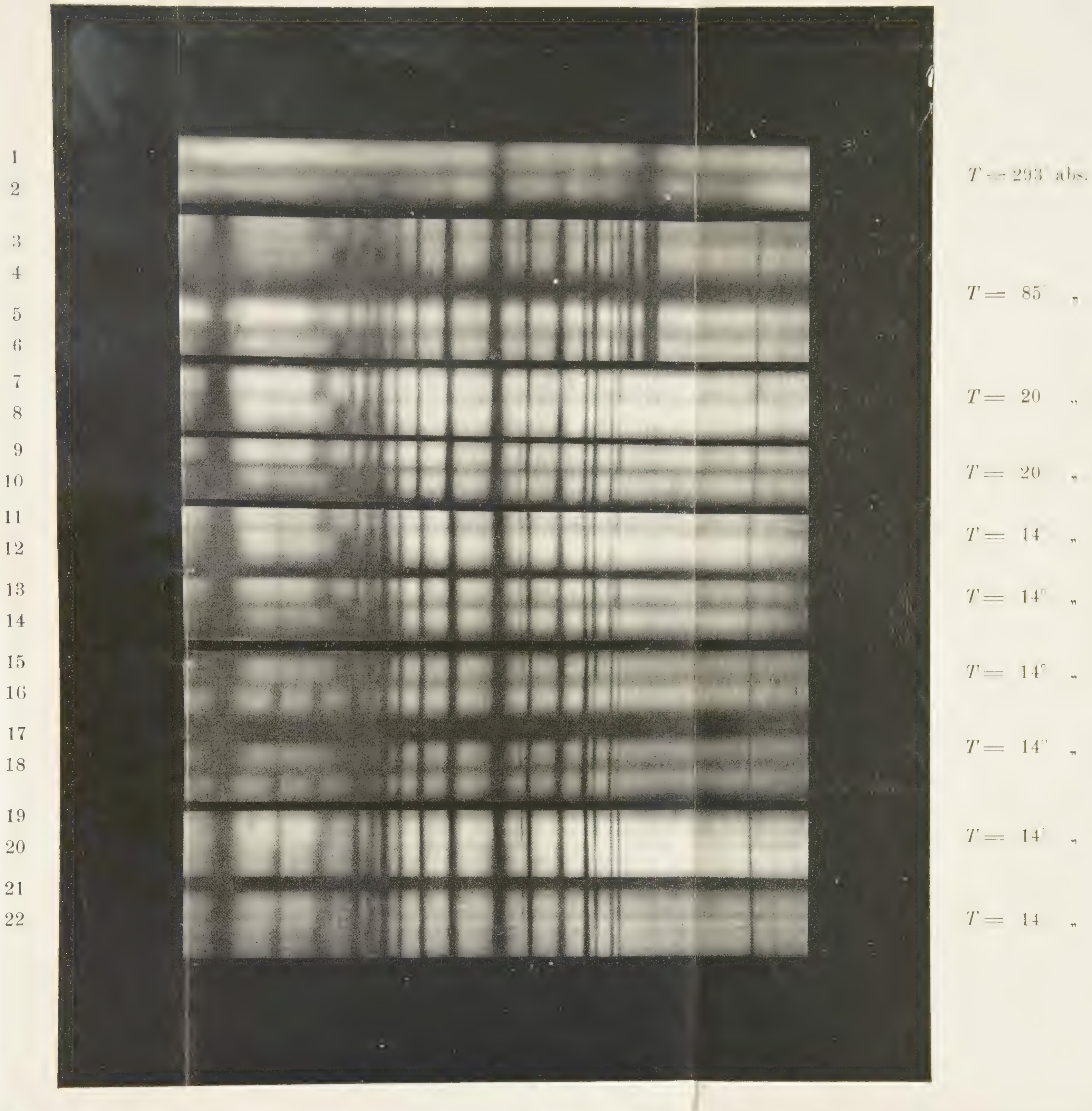

Fig. 7. *Sulphate of neodyme*; specta of vibrations in the directions α β,γ, group in the blue, 2d spectrum (Rowland grating).

| | |
|---|---|
| 1, 3, 7, 11, 19 | α without field |
| 2, 4, 8, 12, 15 | β „ „ |
| 16, 20 | γ „ „ |
| 5 and 6, 9 and 10, 13 and 14 | α and β normal to field (18000 Gauss) |
| 17 and 18 | β and γ „ „ „ „ |
| 21 and 22 | α and γ „ „ „ „ |

Communication No. 103.

**JEAN BECQUEREL and H. KAMERLINGH ONNES.** "*The absorption spectra of the compounds of the rare earths at the temperatures obtainable with liquid hydrogen, and their change by the magnetic field*".

§ 1. *Introduction.* The investigations of one of us (J. B.) [1]) proved that the absorption spectra of the compounds of the rare earths, cooled down to the temperature of liquid air, may serve to acquire new data for the nature, the number, and the motion of the electrons which play a part in the formation of these spectra. So it seemed to us of great importance to continue these investigations at the temperatures obtainable with liquid hydrogen, which are so many times lower and seem particularly adapted [2]) to reveal the forces which the ponderable substance exerts on the electrons. For this purpose the apparatus used at Paris for the observation of the spectra were conveyed to the cryogenic laboratory at Leiden, so that we were enabled to obtain some three hundred of spectrograms which represent the observed phenomena. The study of these photographs will take a long time; we shall therefore confine ourselves on this occasion to the communication of some facts which immediately draw the attention.

§ 2. *Apparatus.* In the first place a few words about the arrangement of the experiments. It was the same for the experiments without and with the magnetic field. The crystals, fixed with wax on a small piece of platinum foil $a$ ($a_2$, $a_3$ fig. $5^a$ Pl. I), which was carried by a rod $a_4$, were immersed in liquid hydrogen in a double-walled tube ($b$ fig. 2, fig. $3^a$), which is the continuation of a non-silvered vacuum glas $b_2$, which contained liquid hydrogen and which is surrounded by another double-walled ($c_{10}$, $c_{20}$) tube $c$, also the continuation of a non-silvered vacuum glass with liquid air, on which it rests on pieces of cork $b_3$. A clearance of $^1/_2$ mm. between the two glasses (fig. $3^a$) proved sufficient to allow the liquid air to circulate along the hydrogen tube. This protects the hydrogen so effectively from access of heat that the evaporation is insignificant, even when the two tubes are placed between the hot coils of the magnet and the crystal is exposed to strongly concentrated electric light.

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[1]) JEAN BECQUEREL. Le Radium IV, 9, p. 328 and IV, 11, p. 385 (1907).

[2]) H. KAMERLINGH ONNES. The importance of accurate measurements at very low temperatures. Comm. phys. lab. Leiden Suppl. No. 9, p. 25 sqq. (1904).

The walls of the narrow part of the tubes are very thin, and because the radiation of heat is independent of the distance of the walls they have been brought to an exceedingly small distance from each other (0.5 mm.), but without being anywhere in concontact. Owing to the skill of Mr. KESSELRING, glassblower of the laboratory, who succeeded in doing this, we had at our disposal a tube of 4 mm. inner diameter filled with liquid hydrogen, protected by a tube of liquid air, the outer diameter of which is no more than 8 mm., which allows us to bring the poles of the magnet so near together that very strong fields are obtained even with hollow poles [1]).

The hydrogen tube must be closed hermetically. For this purpose it is fastened in a cap, $d$, which may be adjusted by means of a levelling board, $f$, with screws and sliding groove. The tube is brought from below into the cap, where it rests against a wooden cylinder, within $d_0$ (fig. 2), and it is fastened with a thin rubber ring $e_1$, which lies round $d_0$ doubled over and is turned down when the tube is put in. To ensure tightness a rubber solution is put between ring and glass, and the rubber is pressed tight against the glass and the cap with copper wire. The cap is provided with: 1. the tube $d_{30}$, to which at $d_{31}$ a head with packing cap $d_{32}$ is screwed, in which the rod $a_6$ can turn (by means of $a_7$), and move up and down (by means of the nut $d_{33}$); 2. a tube $d_1$ to siphon over liquid hydrogen as indicated in Comm. N$^0$. 94 from the supply bottle into the apparatus, which tube is closed in other cases with a rubber tube with cock; 3. an outflow tube $d_2$ (fig. 2), which leads along cock $k$ (fig. 1 and fig. 4) to the gasholder with pure hydrogen, to a safety tube $l$ (fig. 1), along $k_2$ to an airpump, and past $k_4$ to the vacuum bottle $r$, from which the liquid hydrogen is siphoned over (the operation is elucidated by the diagrammatic fig. 4, which does not call for a further description).

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[1]) Instead of the usual poles of the WEISS magnet we have used auxiliary pieces, $p_{30}$ (see figs. 2 and 3), which prolong the cone to a section of 6 mm. diameter, with conic perforations, which have a diameter of 3 mm. on the side of the crystal.

We first have convinced ourselves that when the air has been exhausted from the hydrogen tube surrounded by $c$, this tube exactly occupies its place between the poles, without being strained by the supports $q$ and $i$, when these have a suitable position; we then fill it along $k_1$ with hydrogen from the gasholder, exhausting it repeatedly, then we pour liquid air through a funnel with filter into $b_1$, which is covered with some cotton wool. The apparatus is then filled with liquid hydrogen through $d_1$. In order to pass to the melting point of hydrogen, $k_2$ is opened till crystals appear on the surface of the liquid hydrogen, through which the gas bubbles which rise from the heated crystal, are seen to make their way. If the apparatus has been filled in the way described before, observations with the crystals may be made uninterruptedly for several hours. The precautions taken to prevent mixing of hydrogen and air are indispensable. Air entering the apparatus, would sink down, and be sucked up in front of the crystal as soon as the magnetic field is applied, and intercept the light.

For every filling of the apparatus $\frac{1}{4}$ liter of liquid hydrogen from the supply is generally used, and it was sufficient to do this twice a day to be able to observe all the day in case of ordinary as well as of low pressure; twice a week a quantity of 5 liters was prepared for these experiments, which was just sufficient to fill the apparatus also the second day after the preparation. As it was impossible to entirely prevent the hydrogen which evaporated at lowered pressure from being contaminated with air, it was not admitted again into the cycle. The hydrogen cycle proved its reliability by never failing us a single time in all these weeks.

## I. PHENOMENA WHICH DEPEND SOLELY ON THE TEMPERATURE.

§ 3. *Simplification of the spectra.* On cooling to the temperature of liquid air ($T = 85°$) one of us had found[1]) that almost all bands become narrower and divide, some new ones also appearing. In general their intensity increases. The bands which decrease in intensity or which vanish altogether, are exceedingly few in number. The measurements on anomalous dispersion in the neighbourhood of some bands of tysonite had proved that this increase of intensity is not only the consequence of the bands becoming narrower, but also of a modification which, according to the theory of electrons on the supposition of quasi-elastic forces, indicates the increase of the dielectric constant in every band, and implies that the number of electrons which determine such a band, has increased.

Passing to the temperature of liquid hydrogen ($T = 20°$), we saw some bands continue to increase in intensy, but also others which showed an increasing absorption with fall of temperature down to that of liquid air, decrease both in intensy and in breadth. There are even bands having appeared in liquid air, which become almost invisible in liquid hydrogen. An example of such a change with the temperature is furnished by the bands 523.5 and 479.1 of tysonite.

The measurements of the anomalous dispersion in the neighbourhood of these bands had shown that the electrons belonging to these bands are about twice or three times as numerous at the temperature of liquid air as at the ordinary temperature. In liquid hydrogen the number has already become very small, and at the temperature of solid hydrogen (14°) hardly any electrons of this kind take part in the motion. Fig. 1, Pl. II, which represents the compensator fringes[2]) in the neighbourhood of band 523.5 of tysonite at different temperatures and with different thickness, allows us to measure the disturbance in the fringe with regard to height and breadth. Figs. 2 and 3, which we treat in § 8 and 9, and which represent the magneto-optic phenomena, may elucidate this.

§ 4. *Maximum of intensity of every band for a definite tempe-*

---

1) Jean Becquerel, l. c.

2) Jean Becquerel, Le Radium IV, No. 9, p. 328.

*rature.* It follows from the foregoing that several bands pass through a maximum of intensity with decrease of the temperature. In general the place of this maximum is different for different bands. When in the experiment with tysonite described in § 3 we wait till the last traces of hydrogen evaporate from the crystal, immediately after, when the temperature of the crystal rises, the band 523.5 is seen to greatly increase in intensity. Without doubt the maximum for this band lies at a temperature not far above the boiling point of hydrogen. All the crystals of xenotime, tysonite, parisite, apatite, monazite, didymium sulphate, praseodymium sulphate, neodymium sulphate, exhibit similar phenomena. The green line 523.5 of neodymium which is exeedingly fine and sharp at $T = 20°$, has almost vanished at $T = 14°$.

We have further examined the influence of the fall from $T = 91°$ to $T = 58°$ by immersing the crystals in liquid oxygen boiling at the airpump. The change in this region is only slight. This confirms the conclusion drawn from what was observed in heating from $T = 20°$ upwards, that the maximum must lie near this latter temperature and at all events far below $T = 58°$.

Naturally the question obtrudes itself whether those few bands, whose intensity diminish between the ordinary temperature and that of liquid air, do not also pass through a maximum either between $T = 290°$ and $T = 95°$, or at a temperature above $T = 290°$. It will be difficult to decide the question, because in consequence of the broadening and overlapping of the bands the change of each of these bands in itself escapes observation 1).

§ 5. *Change in width.* In the previous experiments 2) it had been found generally valid for all bands measured down to the temperature of liquid air, that the width of the bands was proportional to the square root of the absolute temperature. This is

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1) Another question is raised by the bands still increasing at the lowest temperatures. They probably pass through a maximum below $T = 14°$. Under these bands are those, who make their appearance by cooling; they constitute a *low temperature spectrum* nearly invisible at ordinary temperatures (Note added C. R. 23 Mars, 1908).

2) Jean Becquerel, Le Radium IV No. 9 p. 328.

the law which for the case of a gas may be deduced from the formulae formerly developed by LORENTZ[1]).

When we pass to the temperature of liquid hydrogen this law appears to be no longer valid for some bands, whereas for others the order of magnitude of the change seems to remain the same. In the figures 1, Pl. II, obtained by the method of the compensator fringes, it is very clearly to be seen[2]), that 523.5 of tysonite is not half as broad at $T = 20°$ as at $T = 85°$, as the law of the $\sqrt{T}$ would require. And it was this very band which had served to show experimentally, that this law held down to $T = 85°$ with a high degree of approximation,

The question whether there is a *minimum of width*, could not be solved yet. At first sight some bands do not seem to contract any further between $T = 20°$ and $T = 14°$, two of xenotime seem even to get wider.

With regard to the totality of the phenomena of change of width in liquid and solid hydrogen we may further remark that in these even more than in liquid air[3]) the spectra manifest a pronounced tendency to assume the character of gas spectra when the temperature decreases. Some absorption lines of praseodymium and neodymium sulphate, cleared of broad bands that covered them, are even finer than the $D$-lines.

§ 6. *The approach to a limit of the double refraction of crystals in the non absorbed parts of the spectrum.* If we watch the bands, by the aid of which the double refraction is investigated, with change of temperature, we observe the following. It the crystal is heated above the ordinary temperature, they are greatly displaced. When the temperature is lowered to that of liquid air they move in the opposite direction. For a crystal of tysonite we have also examined them with further cooling with liquid hydrogen. In spite of the great difference of temperature the displacement is then

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1) H. A. LORENTZ. Zittingsversl. Kon. Akad. v. W. VI p. 506 and p. 555 (1898).

2) In comparing the spectrum 2 of Fig. 1, Pl. II, with those at the other temperatures, attention must be drawn to the difference of thickness of the plates, as is given in the description at the bottom of the figure.

3) That tysonite and xenotime have this tendency has been noted by JEAN BECQUEREL, Le Radium l. c.

hardly perceptible. This may point to the fact that the difference of the expansion of the crystals in the different directions approaches a limit at very low temperatures.

§ 7. *Connection of the change of the absorption bands occurring at very low temperatures with the electronic theory.* Already in § 3 we pointed out the connection of the change of the bands with that of the number of the electrons which are concerned with a certain band according to the electronic theory coupled with the assumption of quasi-elastic forces. The experimental problems raised by § 3 and § 4 may be defined as follows in the language of this theory [1]): to determine as functions of $T$ on one side the number and on the other side the damping coefficient (proportional to the width of the band) of the electrons which belong to a certain band. We might make use of the position of the maxima to find mutually related bands, in the first place in the different spectra of one crystal. An investigation into the connection between what we already know about these functions and what the change of the electrical resistance of the metals [2]) leads us to expect about the action of forces exercised by the ponderable substance on the electrons naturally suggests itself [3]). At very low temperatures we shall no longer be justified in considering the electrons as a perfect gas, but we shall rather have to compare them to a vapour which precipitates on parts of the atoms (dynamides (LENARD)), and solidifies at still lower temperature [4]). When they approach these centres the paths of the electrons are subjected to changes which modify the length of free path in the same way as VAN DER WAALS's quantity $b$ is subjected to a change by the forces exerted by the molecules on each other [5]).

The three states of aggregation which we used just now as an illustration of the behaviour of the electrons, might perhaps be considered as referring to the stability of different paths of the

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1) Cf. JEAN BECQUEREL. Le Radium l. c.

2) Comp. H. KAMERLINGH ONNES and J. CLAY, Comm. Nos. 95*c*, 95*d*, 99*c*.

3) H. KAMERLINGH ONNES. Loc. cit.

4) A metal would become transparent at very low temperature.

5) Calculated by REINGANUM according to the theory of BOLTZMANN.

electrons, and the quasi-elastic force might be connected with the conditions for the electrons moving in these paths.

If we further note that it is the ratio of absolute temperatures on which the degree of change of the spectra depends (compare the transition from $T = 20$ to $T = 14$ with that from $T = 290$ to $T = 95$), we may accept for the present as a heuristic image the idea that we may speak of corresponding states according to different units of temperature caused by mechanic similarity of the motion of the electrons round the centres.

## II. PHENOMENA DEPENDING ON THE TEMPERATURE AND ON THE STRENGTH OF THE MAGNETIC FIELD.

### § 8. *Constancy of the change of the frequency of vibrations under the influence of the magnetic field at all temperatures.*

According to the experiments made by one of us previously (J. B.), when a uniaxial crystal is placed with its axis in the direction of the lines of force and of the ray of light, some absorption bands are resolved into two components, which belong to the absorption of two circularly polarized rays of opposite sense. The difference of frequency of vibration of the two components had then proved to be independent of the temperature. It follows now in a still more convincing way from the comparison of the divergence of the two bands at the temperature of liquid hydrogen with the divergence at the temperature of liquid air, that within the limits of errors of observation, the difference of frequency of vibration is entirely independent of the temperature. According to the theory of LORENTZ this constancy of the divergence of the bands, which is observed both for those which behave in the sense of the ZEEMAN-effect as for those which behave in opposite sense, must be considered as proceeding from the invariability of the ratio $e/m$. Accordingly the observations in liquid hydrogen seem to furnish a strong support to the argument in favour of the existence of positive electrons derived from the constancy of this quotient 1).

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1) Le Radium tom. V. p. 17. 1908. If the bands are caused by negative electrons one would have to suppose that they vibrate in a magnetic field opposed to the outer field, and it is difficult to admit that the inner field would be totally independent of the temperature (Note added C. R. 23 Mars, 1908).

§ 9 *Partial polarisation of the components of some bands.* In a foregoing communication (C.R. 19 Aout 1907) one of us (J B.) has demonstrated, that the band 624.97 of tysonite becomes double in each of the two spectra of left-handed and right-handed circularly polarized light, which are obtained by means of a plate of a quarter wavelength and a rhombohedron. Therefore in both components of the magnetic doublet of the band the polarisation is not perfectly circular. The band behaves as if it were owing both to positive and to negative electrons with the same period of vibration, and the same ratio $e/m$, in which the number of positive electrons is to be put as the largest, because the strongest component belongs to it.

At the temperature of liquid hydrogen the same phenomenon is observed with some bands which become at the same time fine and bright (fig. 2 Pl. II band 522.1). In general the same thing is found on reexamining the spectra at the temperature of liquid air and at the ordinary temperature, though it is more difficult to see. Some time ago DUFOUR again found the same phenomenon in emission bands of fluorcalcium put into the flame.

§ 10. *Asymmetry of the right- and left-handed components.* The experiments at the temperature of liquid air had proved [1] that when the rays of light run parallel to the lines of force the right- and left-handed components very often differ in strength. No regularity had been found in these differences, the asymmetry was now in one, then in the other sense.

If we pass to the temperature of liquid, or better still, to that of solid hydrogen, the asymmetries. which sometimes change their sign, become exeedingly great; one component increases in intensity at the expense of the other, even to such a degree, that some components on the side of the greater wavelengths vanish almost entirely. An example is furnished by fig. 3, Pl. III, referring to 654.2 and 643.4 of xenotime, one component of which is very intense, the other very faint. Apatite shows the same thing.

In solid hydrogen almost all the components which diverge towards the small wavelengths, become very sensibly intenser than those of opposite sign.

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[1] JEAN BECQUEREL. Le Radium V. No. 1. p. 9. 1908.

§ 11. *Variation of the magnetic rotation of the plane of polarisation in the neighbourhood of the absorption bands.*

*a. Simple bands.* The experiments of MACALUSO [1]), H. BECQUEREL [2]), ZEEMAN [3]) have proved that in the neighbourhood of the bands which exhibit the ZEEMAN-phenomenon, the rotation of the plane of polarisation on both sides of the band is positive, and in the inside of the magnetic doublet negative. The experiments made with uniaxial crystals [4]) with the axis placed parallel to the lines of force and to the beam of light either at the ordinary temperature, or at the temperature of liquid air, have proved that the regular change of the magnetic rotatory power with the wavelength of the light is subjected to a disturbance of the same kind on both sides of the band, and to an opposite disturbance at the middle of the band. This disturbance is positive outside the band for the bands belonging to negative electrons, and negative for the bands of positive electrons

At the temperatures of liquid and solid hydrogen the same phenomena are observed, at least when the asymmetry of the left- and right-handed components is not too large. In the neighbourhood of some bands whose components are vere unequal, opposite disturbances are observed on both sides of the band — as is easily explained by means of the usual figures of the anomalous dispersion. These phenomena are clearly visible on the figures 4 Pl. III and 5 Pl. IV.

These figures have been obtained by a method which was already used in former experiments [5]). Against the slit of the spectroscope a BABINET compensator was fixed between two crossed Nicols in such a way that the fringes were perpendicular to the slit. Before the compensator a plate of a quarter of a wavelength is placed in such a way that the two opposite circularly polarized vibrations are changed into two rays rectilinearly polarized parallel and normal to the principal direction of the compensator. The deviations of the fringe in the spectrum in the neighbourhood of the bands are proportional to the difference of phase of the circularly polarized rays in the crystal plate.

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[1]) C.R. CXXVII p. 548. 1898.

[2]) C.R. CXXV p. 679. 1897. CXXVII p. 899 1891.

[3]) Arch. Néerl. VII p. 465. 1902.

[4]) JEAN BECQUEREL, Le Radium IV No. 2 p. 49, 1907, V No. 1 p. 5, 1908.

[5]) JEAN BECQUEREL, C.R. 21 Mai, 1906.

In the figures we find for band 522.15 fig. 4 the symmetrical case, for band 523.7 fig. 4, and 642.3 fig. 5 the dissymmetrical case with disturbance in the same direction, for band 537 fig. 4, and 654.2 fig. 5 the opposite disturbance on both sides of the band.

*b. Compound bands.* The phenomena of absorption at lower temperatures have shown that several bands may be resolved into two or more. These components behave differently with respect to the magnetic field, because some belong to positive, others to negative electrons. Therefore we meet with disturbances in the magnetic rotation which are different for the different bands, and whose effects are superposed. Thus two bands placed side by side, one of positive and the other of negative electrons, may give rise to disturbances in opposite direction in the dispersion of magnetic rotation. It is perhaps to this that we must look for the explanation of what is observed in band 577 of tysonite, which is clearly double in liquid hydrogen.

In general we may say that with regard to the theory of the magnetic rotation for absorption bands, the conclusions drawn from experiments at the ordinary temperature do not lead to a definite result. For at the ordinary temperature it is uncertain whether we have really to deal with a simple band. On the other hand at the low temperatures, at which the bands become narrow, and their change in the magnetic field may be closely followed, it is easy to find the true explanation of the different types of disturbances in the magnetic dispersion of rotation for the bands in the different cases.

§ 12. *Magnetic rotatory power of the paramagnetic crystals.* One of us (J. B.) [1]) had previously shown that the negative magnetic rotatory power of the crystals of tysonite and parisite increases considerably with decrease of temperature The rotatory power is about inversely proportional to the absolute temperature. If this is brought into connection with the law of CURIE that the paramagnetic susceptibility is inversely proportional to $T$, it appears that the negative rotation of these crystals is probably a consequence of the increase of the paramagnetic polarisation of the crystal.

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[1]) Jean Becquerel, Le Radium. V N⁰. 1, p. 5, 1908.

If these crystals are placed in liquid hydrogen we find that the increase continues in the same way with decrease of temperature, and the rotatory power rises to exceedingly high values. The exact numbers will be given later, but in round numbers the rotation of the plane of polarisation of the blue light amounts to 150° for a plate of tysonite of 1 mm. in a field of 10000 Gauss at the boiling point of hydrogen. Xenotime, which gives a very slight rotation at the ordinary temperature, shows a considerable rotatory power in liquid hydrogen.

### § 13. *Connection between the phenomena of the asymmetry of the left- and right-handed polarized components by the magnetic field at very low temperatures, and the electronic theory.*

In connection with § 4 the phenomena taken together give rise to the supposition that for the paths of the electrons there exist conditions (fields) of stability, which are determined by the temperature. The action of the magnetic force and the change in the rate of vibration would then bring about that some electrons enter these fields of stability or leave them, both changes occurring either in the direction of greater union with or further separation from the centres which determine the paths, and the increase of this action at low temperature would be in connection with the small velocity. The influence on the stability of the paths, which is here considered, would be the same as manifests itself in the change by temperature of the number of electrons (see § 7) which satisfy the conditions of the motions which may be ascribed to quasi-elastic forces.

In this connection the question suggests itself if the greater stability of vibrations in a certain direction will not give rise to paramagnetic properties.

§ 14. *Variability of the mass of the electrons with the direction of the movement.* The theory of the magneto-optic phenomena in crystals (Voigt [1]), Jean Becquerel [2]) ) leads to the following results.

The magnetic field gives rise to certain connections between the motions of the electrons in the different principal directions of the crystal. Let us consider the simple case which is repeatedly met with, viz. that the corresponding bands in the different spectra occupy the same place. In that case according to the theory the magnetic doublets will have to be symmetrical, and when the bands are sufficiently narrow to allow us to neglect the breadth, the deviations will be proportional to the square root of the product of the two magnetic constants which belong to the corresponding bands of the two spectra If the beam of light and one of the principal directions 1, 2, 3 of the crystal are made to coincide with the direction of the magnetic field, those two of the three spectra of the crystal are observed which correspond with the vibrations normal to the lines of force.

Observation shows that both for the uniaxial crystals of xenotime and tysonite and for the biaxial crystals of didymium sulphate, neodymium sulphate, and praseodymium sulphate (which last exhibits some lines in liquid hydrogen as sharp as vapour lines) the doublets of the common band have the same divergence. A phenomenon of great importance is observed, when the spectra of vibrations normal to the lines of force are combined in different ways. If the directions 1, 2, 3 successively are placed in the directions of the field, we get the combinations 2.3, 1.3, 1.2 for the vibrations normal to the field. Experiment shows that the divergences of the pairs of doublets in these three cases are very different. Thus for a band of spectrum 1, the vibration being normal to the field, the magnetic doublet is different according as the direction normal to the field has the principal direction 2 or 3. The phenomenon is clearly seen in the figure which represents the group of bands in the orange for neodymium sulphate at — 259°. Fig. 7 Pl. V gives a survey of the phenomena of the changes with the temperature and the magnetic field in the blue of neodymium sulphate. According to theory it follows from this that each of the three different directions has a different magnetic constant, and that therefore the vibrating system presents three different masses [1]) for the three kinds of vibrations.

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[1] Nachr. Kön. Ges. d. Wiss. Göttingen Juli 1906.

[2] C. R. 19 Nov., 3, 10, 24 Déc. 1906, Le Radium IV N⁰. 3, March 1907.

As the corresponding bands in the two spectra occupy the same or only slightly different places, it follows that in first approximation the constant of the quasi-elastic force in each of the three directions must be proportional to the mass in that direction.

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1) This could be the result of an ellipsoïdal shape of the electron (Note added C. R. 23 Mars, 1908).

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,
*Director of the Laboratory.*

## No. 104a.

**Dr. H. KAMERLINGH ONNES and Dr. W. H. KEESOM.**
"On the equation of state of a substance in the neighbourhood of the critical point liquid-gas. I. The disturbance function in the neighbourhood of the critical state." (*With a plate*).

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam,* **29 Februari 1908**, p. 659—666).

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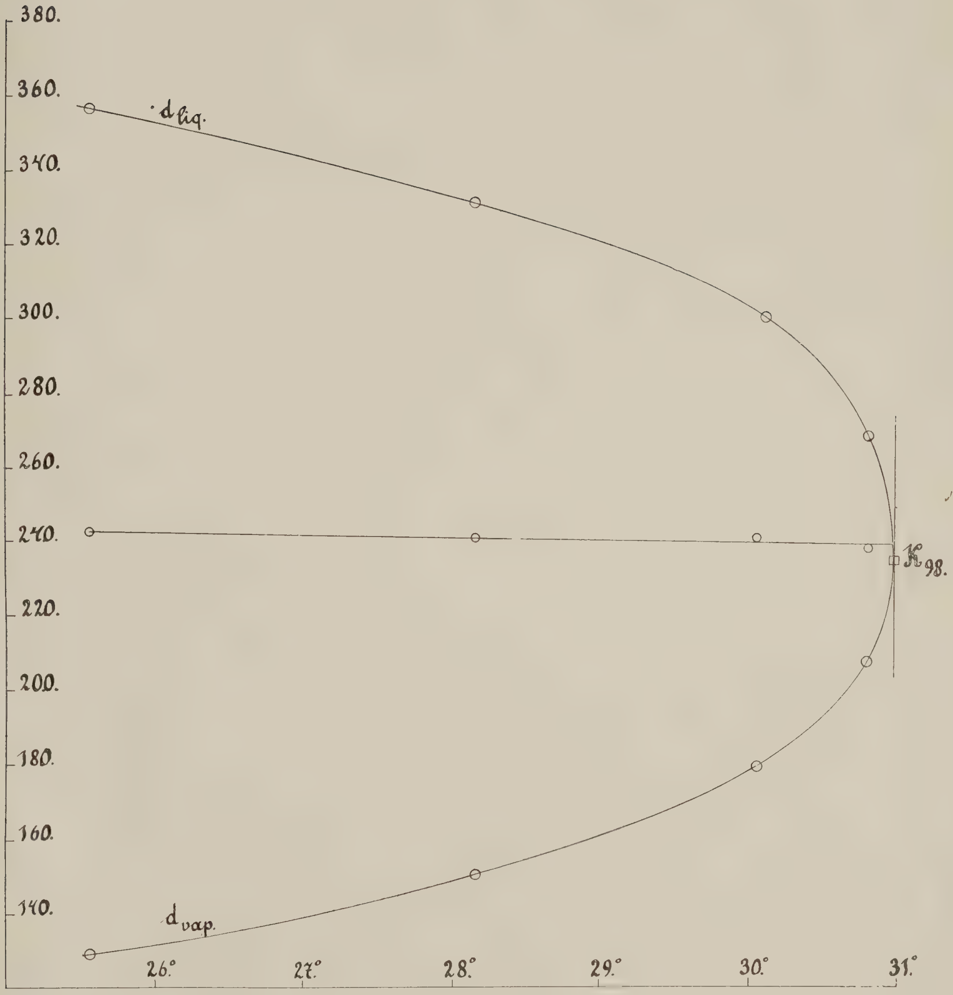
Dr. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. "On the equation of state of a substance in the neighbourhood of the critical point liquid-gas. I. The disturbance function in the neighbourhood of the critical state."

Plate I.



Communication N$^{o}$. 104$^{a}$.

## **Dr. H. KAMERLINGH ONNES and Dr. W. H. KEESOM.** "*On the equation of state of a substance in the neighbourhood of the critical point liquid-gas.* I. *The disturbance function in the neighbourhood of the critical state.*"

§ 1. The great compressibility of a substance in the neighbourhood of the critical point liquid-gas and the properties connected with this, (such as the small variation of the thermodynamical potential at isothermal compression etc.) — which are derived from VAN DER WAALS's original equation of state and better still from his latest considerations about the compressibility of a molecule [1]) — render it necessary that in deriving conclusions from observations in the neighbourhood of that condition we must take into account various circumstances, which otherwise for the experimental investigation of the equation of state of a homogeneous substance consisting of one component, which investigation includes that of the quantities of saturation etc., need not be considered.

It is well-known that owing to the great compressibility the thermodynamic equilibrium is difficult to attain, in fact it has often happened that phenomena at the critical point have been described as abnormal [2]) and as being at variance with the views of ANDREWS-VAN DER WAALS, in cases where the thermodynamic equilibrium had not yet been attained either because small differences in composition had remained owing to the slow diffusion of very small quantities of admixture (KUENEN, Comms. N°. 8, Oct. '93, N°. 11, May and June '94), or because differences of temperature resulting from variations of volume in different portions of the substance during the passage from one condition of temperature and pressure to the next had not yet been equalized (KAMERLINGH ONNES, Comm.

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[1]) Comp. VAN DER WAALS, Proceedings Kon. Akad. v. Wet. Amsterdam, June '03.

[2]) For a survey of these phenomena comp. GRAETZ, WINKELMANN's Handbuch, III, 2te Aufl. p. 837.

N°. 68, March and April '01 and KAMERLINGH ONNES and FABIUS, N°. 98, May '07).

When the thermodynamical equilibrium is obtained either by keeping the substance in the neighbourhood of the critical point during a long time at a constant temperature, or by repeated reversals of the sealed tube containing the substance (GOUY), or by stirring it electromagnetically (KUENEN), we must pay regard to the gravitation which on account of the great compressibility of the substance in that condition becomes of great influence [1]) and also to small quantities of admixture which may occur and of which the nature and the quantity are known [2]).

The consideration of these influences and those of capillarity and absorption phenomena near the walls of the vessel [3]), things which in other cases are hardly to be considered, is indispensable at the critical point liquid-gas for the determination of the *experimental equation of state of a substance*, i. e. the relation between $p$, $v$ and $T$ for a substance consisting of one component in thermodynamic equilibrium subject to no other external forces than the pressure of the walls of the vessel.

§ 2. In this communication we intend to bring into connection some peculiarities in the experimental equation of state in the neighbourhood of the critical state with the great compressibility in this area. Therefor we compare the experimental equation of state of a substance near the critical point liquid-gas with an equation of state which we shall call *the special undisturbed equation of state for that substance* and which is derived by adjusting interpolation formulae to observations in areas where no disturbances occur such as in the neighbourhood of the critical point.

For we presume to be able to derive from the results of data at our disposal that the experimental equation of state differs from the special undisturbed one by the presence of terms which for the accuracy reached in the observations meant only deserve notice in the neighbourhood of the critical point, and which are intimately connected with the great compressibility in this area. We shall call the compound of these terms *the disturbance function in the equation of state in the neighbourhood of the critical point.*

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[1]) GOUY, C. R. 115 (1892) p. 720 and 116, p. 1289, J. P. KUENEN, Comm. N°. 17, May '95.

[2]) Cf. Comm. N°. 75, N°. 79, N°. 88 (KEESOM), N°. 81, Suppl. N°. 6, N°. 10, N°. 12 (VERSCHAFFELT). On the influence of gravity a small quantity of admixture being present, cf. KUENEN, Comm. N°. 17 and KEESOM, Comm. N°. 88 VI.

[3]) Comp. VAN DER WAALS, l. c. p. 147.

In order to be able to derive from the special undisturbed equation of state and the disturbance function at the critical state the conditions of coexistence, vapour pressures, liquid and vapour densities, we must have investigated whether in that condition MAXWELL'S criterion for a substance constisting of one component may be applied unmodified or not.

For the present we must include in this disturbance function the disturbances caused by admixtures which chemically may have an existence of their own, but which it was not possible to remove and which always occur in definite quantities, as long as the nature and the quantity of these admixtures are unknown. The investigation of substances with small quantities of admixture ¹) may help us towards a better judgment of the question whether this disturbance function may be entirely ascribed to admixtures which may exist separately. As long as this has not yet been decided it will be indispensable to pay regard also to admixtures which can have no existence of their own but which may always occur as electrically charged particles, or as portions of the substance of greater density which may give rise to differences of density distributed as nebulous drops and which in this area might be kept up by capillary force. It will also be necessary to take into account differences of density depending on the statistic equilibrium.

In order to arrive at some knowledge of such a disturbance function, observations of greater accuracy are required over an area which comprises the critical state and also approaches it sufficiently. These observations must be accurate to within $^1/_{5000}$, as is reached in the Leiden laboratory in the investigations of bi- and monatomic substances and their binary mixtures, while the nature and the

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¹) Comp. p. 4 note 2. For the influence of small quantities of admixture of substances of small volatility the following investigations are important: M. CENTNERSZWER, ZS. physik. Chemie 46 (1903) OSTWALD Jubelb. p. 427, 61 (1907) p. 356; M. CENTNERSZWER and A. PAKALNEET, ibid. 55 (1906) p. 303, M CENTNERSZWER and A. KALNIN, ibid. 60 (1907) p. 441.

quantity of the separable admixtures ought te be kwown to $^1/_{10000}$ of the whole mass [1])

§ 3. Our conclusion about the existence of a disturbance function in the equation of state in the neighbourhood of the critical point liquid-gas is based on the following data which may be arranged into three groups.

*a.* In Comm. N⁰. 74 (Arch. Néerl. (2) 6 (1901) livre jub. BOSSCHA p. 874) has been pointed out that AMAGAT's observations of the isothermals of carbon dioxide near the critical point show systematic deviations from the values derived from the special undisturbed equation of state. This equation of state was derived from the empiric equation of state introduced in Comm. N⁰. 71, by choosing the virial coefficients so (Comm. N⁰. 74 § 4) that the agreement with the observations over the whole area of observations is as good as possible while the agreement with the general reduced equation of state at a reduced temperature lying far outside the area of observation was retained.

We get a similar series of deviations if we compare the observations of carbon dioxide in the neighbourhood of the critical point — described in Comm. N⁰. 88 — with the special undisturbed equation of state, while using the reduced virial coefficients V. s. 1 (Comm. N⁰. 74, p. 12) and the critical temperature and pressure found in Comm. N⁰. 88.

It really appeared in Suppl. N⁰. 14 (KAMERLINGH ONNES and Miss JOLLES) that the critical quantities, derived according to $\partial p/\partial v = 0$, $\partial^2 p/\partial v^2 = 0$ from the special undisturbed equation of state V. s. 1, show great deviations from those derived experimentally.

A similar difference was found by AMAGAT (Journ. de phys. (3) 8 (1899) p. 353) when he derived the densities of saturated liquid and vapour from the equation of state (containing 10 constants) formed by him for carbon dioxide. The curve which represents the densities calculated thus as a function of the temperature, at lower temperatures coincides almost with the curve given by the obser-

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[1] For such an investigation carbon dioxide would be fittest owing to the comparably small difficulties in preparing it perfectly pure and keeping its temperature sufficiently constant, and also because much is already known about its equation of state over a large area.

**Erratum Communication N⁰. 104.**

p. 6 line 1 from the top: for „kwown" read „known".

vations; according as we approach the critical temperature the calculated curve shows a displacement towards the small densities with regard to the observed curve. That this displacement is much larger than follows from the calculation of Suppl. N⁰. 14 mentioned above must be ascribed at least partly to the circumstance that AMAGAT probably did not derive the liquid and vapour densities from his equation of state by means of the criterion of MAXWELL, but for shortness' sake calculated by means of his equation of state the densities for which $p$ has the value for the saturation pressure furnished by experiment.

*b.* In Comm. N⁰. 75 attention was directed to the difference between the $C_5 = \left[\frac{T}{p}\left(\frac{\partial p}{\partial T}\right)_v\right]_k$ derived from AMAGAT's net of isothermals and the $C_6 = \left[\frac{T}{p}\frac{dp_{coex}}{dT}\right]_k$ resulting from his determinations of the saturated vapour pressure, which values must be equal for the undisturbed equation of state [1]). One of the reasons to undertake the observations about carbon dioxide of Comm. N⁰. 88 was the wish to obtain more certainty about these peculiarities in the behaviour of the substance in the neighbourhood of the critical point (comp. l. c. p. 42). The same difference viz. $C_5 = 7.12$, $C_6 = 6.71$ followed from these determinations. BRINKMAN (Thesis for the doctorate, Amsterdam 1904, p 43) confirmed this difference not only for carbon dioxide, but he also found it for methyl chloride, whereas MILLS (Journ. phys. Chem. 8 (1904) p. 594, 635; comp. also 9 (1905) p. 402) for ethyl oxide (RAMSAY and YOUNG), isopentane and normal pentane (YOUNG) finds differences of 10 percent between $C_6$ derived by means of the formula of BIOT for the saturated vapour pressures and $C_5$ which with regard paid to the regular variation of $b$ with temperature [2]), follows from the data collected by RAMSAY and YOUNG (ethyl oxide), YOUNG (isopentane) and ROSE-INNES and YOUNG (normal pentane) in order to judge of the equation of isochors $p = b\,T - a$.

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[1]) M. PLANCK, Wied. Ann. 15 (1882) p. 457; comp. also Comm. N⁰. 75 § 3. The quantities $C_5$ and $C_6$ are both obtained by an extrapolation, $C_5$ at $v = v_k$ from a higher temperature to $T_k$, $C_6$ along the vapour pressure curve from lower $T$ to $T_k$.

[2]) S. YOUNG, Proc. Phys. Soc. London 1894/95, p. 602; comp. also Comm. N⁰. 88 p. 54 note 1.

*c.* In Comm. N⁰. 88, p. 52 table XXII the saturated vapour pressures of carbon dioxide between 25°.55 C. and the critical temperature (30°.98 C.) are compared with the formula $log\,\frac{p}{p_k} = f\,\frac{(T - T_k)\,T_k}{T^2}$ which was obtained by keeping in the development of *log p* in ascending powers of $T^{-1}$ the second power (1). While for the other temperatures in the table mentioned the deviations did not exceed 0.01 atm., a deviation of Obs. — Calc. = 0.05 atm. was found for 30°.82 (2) (3). Although it was then held probable that this deviation was to be ascribed to an accidental error of observation, we have afterwards found that a deviation in the same sense and of about the same size also occurs in the results of other observers about saturated vapour pressures of carbon dioxide near the critical point.

A comparison of the results of Brinkman's observations (Thesis, Amsterdam 1904 pp. 41 and 42) on saturated vapour pressures of methyl chloride and carbon dioxide with the pressures derived by him according to a formula of the same form as the one mentioned above, yields the following differences:

for methyl chloride ($t_k = 143.°12$):

at $t$ = 137.°54, 138.°92, 140.°26, 141.°66, 142.°02
O—C = + 0.02, — 0.01, — 0.02, + 0.03, + 0.08;

for carbon dioxide ($t_k = 31.°12$):

at $t$ = 24.°24, 26.°08, 28.°46, 29.°86, 30.°40
O – C = + 0.02, — 0.02, + 0.03, + 0.08, +0.07.

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(1) In Physik. ZS. 8 (1907) p. 944, Bose went still farther and kept the third power in this development which had been given by Rankine, Misc. Scientif. Papers pp. 1 and 410.

(2) As it appears from the columns Obs. and Calc. all the numbers in the column O—C have wrong signs.

(3) From the determinations of the saturated vapour pressure in the neighbourhood of the critical state a tendency of $f$ becoming infinite, as von Jüptner, ZS. physik. Chem. 60 (1907) p. 101, supposes, cannot be derived. Moreover, such a behaviour of $f$ is not te be deduced from the known properties of the $p, v, T$-surface (cf. Comm. N⁰. 75 § 3, 3⁰), nor is it probable with regard to the thesis $C_5 = C_6$ (p. 7) for the undisturbed equation of state, whereas the disturbance in the neighbourhood of the critical point tends in the other direction.

For both substances investigated one finds below the critical temperature an obvious deviation resembling that found in Comm. N⁰. 88.

The observations of AMAGAT, Journ. de phys. (2) 1 (1892) p. 288, on the saturated vapour pressure of carbon dioxide fail to give any definite indication about the question treated here because AMAGAT has rounded off the pressures to 0.1 atm. In connection with the preceding statements, however, it deserves attention that TSURUTA, Journ. de phys. (3) 2 (1893) p. 272, when comparing these data with the formula $p = 34.3 + 0.8739t + 0.01135t^2$, also there found an obvious difference O – C at 31.°25 which exceeds by 0.06 atm. that at 31.°35 (crit. temp. according to AMAGAT).

From the data mentioned here one might draw the conclusion that for carbon dioxide and methyl chloride the curve of the saturated vapour pressures, continued to near the critical point, with extrapolation to this point would lead us to expect a $p_k$ somewhat larger than the critical pressure found experimentally. From the very careful observations of YOUNG on isopentane, Proc. Phys. Soc. London 1894/95, p. 613, however, a deviation as found above for carbon dioxide cannot be derived.

It may be that some connection exists between the above mentioned disturbance in the saturation pressure in the immediate neighbourhood of the critical point of carbon dioxide and a disturbance in the observations of Comm. N⁰. 88 of the densities of saturated liquid and vapour of carbon dioxide. Plate I represents these densities $d_{liq}$ and $d_{vap}$, expressed in theoretical normal density. $\frac{1}{2}(d_{liq} + d_{vap})$ is also represented. The straight line is the line which was drawn for the determination of the critical volume after the method of the rectilinear diameter of CAILLETET and MATHIAS in Comm. N⁰. 88 (comp. Comm. N⁰. 88 p. 52). The middle of the chord belonging to 30.°8 lies clearly below this line. If for the determination of the rectilinear diameter only the three points at lower temperature are used, the difference is much larger. If this deviation is not to be ascribed to an error of observation, it would follow hence that the diameter of CAILLETET and MATHIAS for carbon dioxide shows a curvature in the immediate neighbourhood of the critical point[1]. $K_{98}$ indicates the critical density which in Comm. N⁰. 98 (KAMERLINGH ONNES and FABIUS) was derived from determinations less than 0.°002 below the critical temperature. If we might assume that the carbon dioxide of Comm. N⁰. 98 and that of N⁰. 88 possessed the same degree of purity, an assumption to which the agreement between the critical temperatures entitles, and also that the difference in the methods of density determination has not given rise to a systematic difference, then the situation of the point $K_{98}$ would confirm the curvature of the diameter in the neighbourhood of the critical point.

A similar disturbance as we remarked above for the saturation volumes of carbon dioxide in the immediate neighbourhood of the critical point, cannot be derived either from YOUNG's observations on isopentane (comp. Proc. Phys. Soc. London 1894/95 p. 636) or from those on normal pentane (Trans. Chem. Soc. 71 (1897) p. 455), which are continued as far as 0°.05 below the critical temperature[2]. It would be very desirable to investigate more closely in how far the disturbances mentioned sub *c* are connected with a disturbance in the equation of state, or must be ascribed to special circumstances of those experiments themselves (such as the difficulty to determine the moment at which begin condensation occurs).

§ 4. The disturbances mentioned in § 3 apparently point to the fact that the substance in the neighbourhood of the critical point occupies a smaller volume than would be expected according to the special undisturbed equation of state. In Comm. N⁰. 88 p. 55 the possibility is mentioned that these disturbances are connected with differences of density which occur in the substance near the critical state, as it is indicated by the mist (the blue opalescence) in the neighbourhood of that state. The question was left aside wether those differences of density are to be interpreted either as condensations round condensation centres with an existence of their own (dust according to Konowalow [1]), electrically charged particles [2]), a third phase separated in small drops and for the greater part consisting of an admixture), or simply as spontaneously formed differences of density, either as accidental aggregations caused by molecular motion and governed by the statistic equilibrium (Smoluchowski [3]), or because small drops still have a positive surface tension at temperatures at which larger drops are no longer stable (Donnan [4]).

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[1] This curvature is in another sense than the curvature found by KUENEN and ROBSON (Phil. Mag. (6) 3 (1902) p. 624) at lower temperatures in the diameter for carbon dioxide and which agrees with the general rule given by YOUNG (Phil. Mag. (5) 50 (1900) p. 291) about this curvature at lower temperatures in connection with the value of $\frac{RT_k}{p_k v_k}$ and the slope of the diameter as compared with the temperature axis.

[2] Nor can a similar disturbance be derived with certainty from BRINKMAN's observations on carbon dioxide and methyl chloride, which observations, however, are not continued so near to the critical point as those of Comm. N⁰. 88.

Whatever may be the cause of the blue mist, in all cases we may expect a close relation between the compressibility and the occurrence of it. In order to form a better judgment about this matter it was considered to be desirable to start an investigation on the conditions of existence of this cloud in a substance consisting of one component in the neighbourhood of the critical point liquid-gas. For an optical research of these conditions of existence we refer to the next communication.

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¹) D. Konowalow. Ann. d. Phys. (4) 10 (1903) p. 360.

²) Owing to the highly penetrating radiation from the radio-active portions of the crust of the earth (Eve, Phil. Mag. (6) 12 (1906) p. 189), in the atmosphere (Strong, Physik. ZS. 9 (1908) p. 117), or in the surroundings of the building where the experiments are made, these particles would always be present to about the same amount. In the meantime it follows from the experiment of Friedländer, ZS. physik. Chem. 38 (1901) p. 385, on the stability of the mist in an electric field, that the particles which cause the opalescence are not electrically charged.

³) M. v. Smoluchowski, Ann. d. Phys. (4) 25 (1908) p. 205.

⁴) F. G. Donnan, Chem. News 90 (1904) p. 139.

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

## No. 104b.

**Dr. H. KAMERLINGH ONNES and Dr. W. H. KEESOM.** "On the equation of state of a substance in the neighbourhood of the critical point liquid-gas. II. Spectrophotometrical investigation of the opalescence of a substance in the neighbourhood of the critical state".

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam,* **29 Februari 1908**, p. 667—678).

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Dr. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. "On the equation of state of a substance in the neighbourhood of the critical point liquid-gas. II. Spectrophotometrical investigation of the opalescence of a substance in the neighbourhood of the critical state."

Plate II.

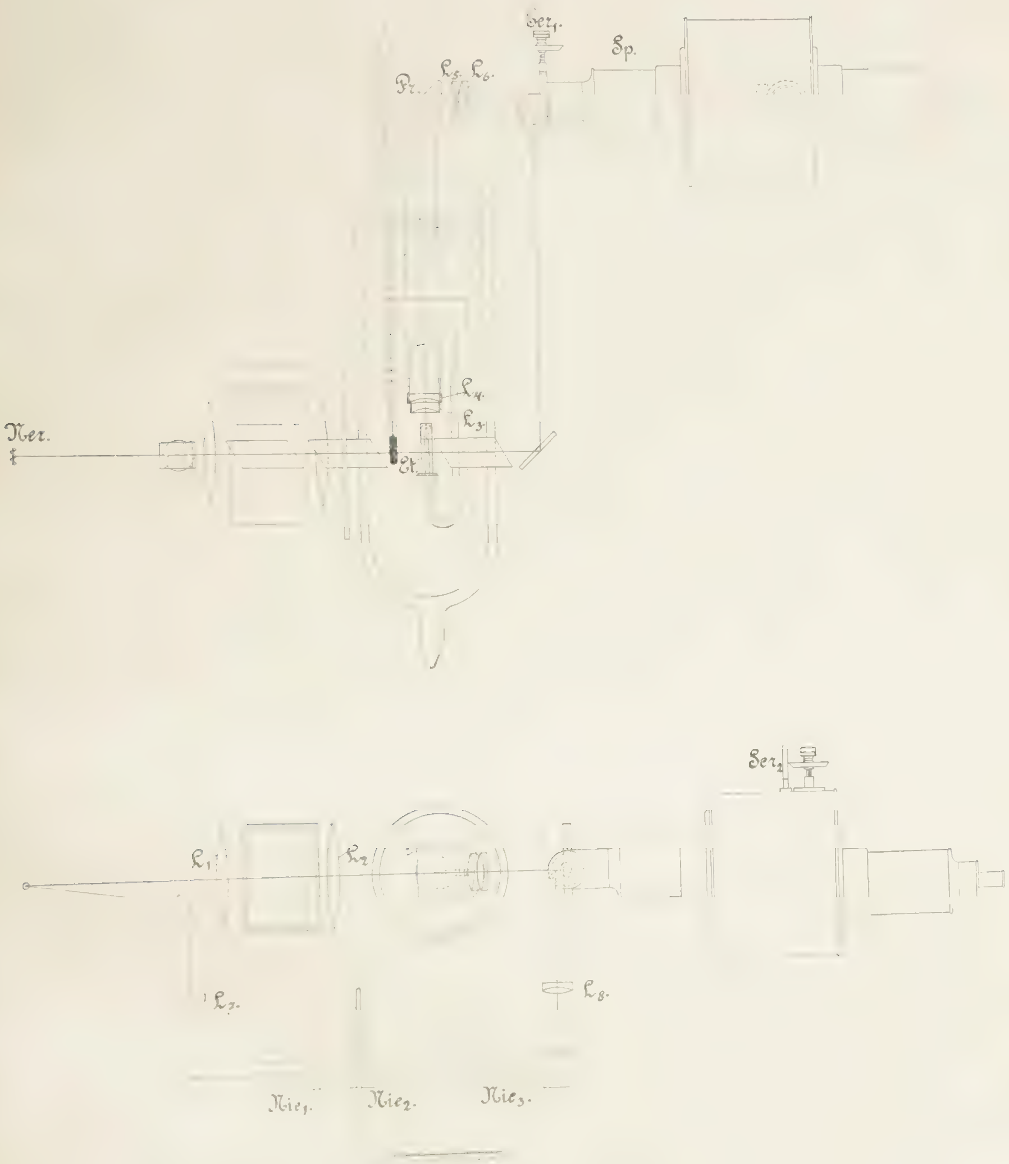

Fig. 1.

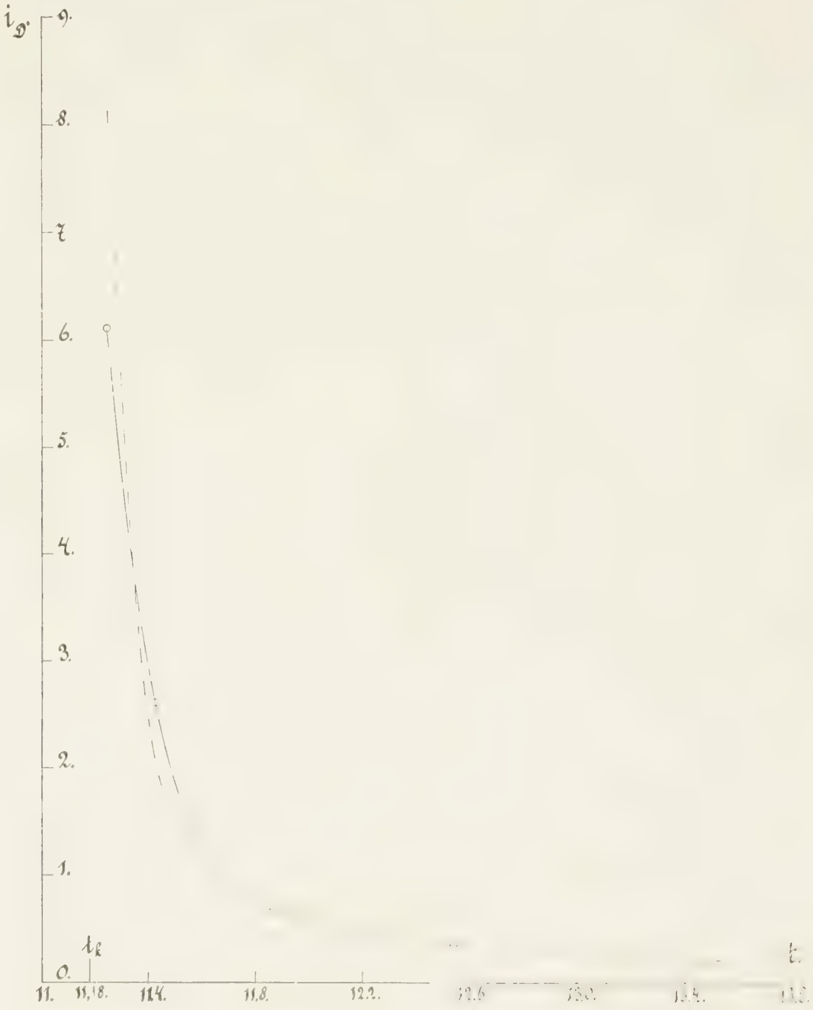

Fig. 2.

Communication No. 104$^b$.

## **Dr. H. KAMERLINGH ONNES and Dr. W. H. KEESOM.** "*On the equation of state of a substance in the neighbourhood of the critical point liquid-gas.* II. *Spectrophotometrical investigation of the opalescence of a substance in the neighbourhood of the critical state*".

§ 1. *Introduction.* The spectrophotometrical investigation [1]) of the opalescence will have to give an answer to the question how the quantity of the light of a certain wavelength scattered in a certain direction with respect to the incident light and included in a certain angle of vision, in connection with the polarisation state depends on the temperature and the density of the single substance in the neighbourhood of the critical point liquid-gas (cf Comm. N⁰. 104*a* § 4). A first quantitative contribution to this investigation is given in this communication [2]).

We have confined ourselves in this first investigation to the determination of:

1. for different temperatures the ratio in which the rays of light of different wavelengths at the same temperature are scattered in a certain direction;

2. the way in which the quantity of the light of definite wavelength scattered in a certain direction and included in a certain angle of vision changes with temperature.

On the supposition *a*, that the light emitted by the blue mist is owing to the scattering of the incident light in consequence of part of the substance condensing to particles of the same size (e.g. spheres) round centres which are uniformly spread through the space, the results of the investigation mentioned under 1 will enable us to form an opinion on the size of these particles [1]), that under 2 on the way in which the total quantity of substance which has condensed, varies with the temperature.

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[1]) This investigation was carried out before the interesting article of Smoluchowski, Ann. d. Phys. (4) 25 (Febr. 7, 1908) p. 205, appeared. We still had an opportunity, however, to compare it with some parts of the text (cf. also the preceding Communication).

[2]) The colorimetric determinations of Friedländer ZS. physik. Chem. 38 (1901) p. 385 constitute such a contribution for a mixture of two liquids in the neighbourhood of the critical point of separation.

On the more general supposition *b*, that the opalescence is the consequence of differences of density e.g. governed by the statistic equilibrium, which extend over parts of the volume of irregular shape and size, a distance can be pointed out which is connected with the average size of these parts of the volume and so with the substance being more or less coarse-grained in that state, and which determines the optical phenomenon in a similar way as the size of the particles on supposition *a*. The investigation mentioned under 1 will then enable us to judge about this distance. When in future we speak of the size of the light-scattering particles, we shall refer to this distance. In this case the investigation mentioned under 2 will teach us something about the mean deviation of the density in these parts of the volume. This too will be implied in future in the terms "the quantity of condensed substance".

The measurements made by us can be only considered as preliminary ones. As, however, we have to put off the continuation of these measurements for some time, we think that we must not postpone the communication of these provisional results any longer.

§ 2. *The arrangement of the experiments* is represented in Pl. II fig. 1. After having passed through a layer of water the light emitted by the glower of the NERNST-lamp *Ner* (70 HK) is concentrated by the lenses $L_1$ and $L_2$ (to an image of ± 1 c M. height) in the tube *Et* filled with ethylene [2]).

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[1]) Already FRIEDLÄNDER loc. cit. p. 438 called attention to the importance of such an investigation for the knowledge of the internal structure of the critically turbid media.

[2]) This was obtained by distilling over so much from the ethylene circulation of the cryogenic laboratory into the glass tube with cock fused to it, which had been cooled in liquid air, and rinsed with ethylene, that after the gas phase left above the solid ethylene had been drawn off, and the tube was heated to the melting point of the ethylene, $^1/_3$ of it was filled. Then with the cock closed the tube was removed from the ethylene circulation, and fused together at a previously narrowed place while still partially placed in liquid air. When the temperature rose to that of the room, it appeared, when at 0° the rime cleared away, that in the

The light scattered upwards in the direction of the axis of the tube [1]) by the cloud is concentrated by means of the system of lenses $L_3$, $L_4$ and $L_5$, $L_6$ and the totally-reflecting prism *Pr* to an image of the beam of light crossing the ethylene tube on the slit of the spectroscope *Sp* (a direct-vision spectroscope of HILGER-CHRISTIE giving a spectrum of great intensity [2]), in which an eye-piece slit has been made in order to confine a certain portion of the spectrum; by means of the screw $Scr_2$ different portions of the spectrum may be brought into the field). A beam of the light emitted by the NERNST-lamp is thrown on the slit of the spectroscope by means of plane mirrors through the polarizing prisms $Nic_1$, $Nic_2$, $Nic_3$ (after having been first made parallel by lens $L_7$) and then through lens $L_8$ and a totally-reflecting prism. The prisms $Nic_1$ and $Nic_3$ are rigid, which ensures that the light thrown into the spectroscope with different positions of $Nic_2$ is reduced in the same proportion by the reflections on the mirrors; the prism $Nic_2$ can turn round, and is provided with a graduated circle, which could be read up to 3′. The plane of polarisation of $Nic_3$ is horizontal so that the condition of polarisation in the two beams thrown into the spectroscope agrees in the main [3]). The plane of

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gas space a thin white deposit was visible on the wall, which evaporated some degrees below the critical temperature of the ethylene. This deposit points to the presence of an admixture which is slightly less volatile than ethylene (cf. VILLARD, Ann. de chim. et de phys. (7) 10 (1897) p. 389). That it was not visible in the liquid space, probably points to a small difference in refrangibility with liquid ethylene.

When we stirred, and then slowly cooled the tube to below the critical temperature, the meniscus appeared in the top of the tube.

[1]) The top of the tube is surrounded by a black cylindre in order to prevent rays of light received by this part from being reflected upwards, and being thrown into the spectroscope.

[2]) See ZEEMAN Comm. N⁰. 5, more detailed Arch. Néerl. 27 (1893) p. 259 and Pl. V. The "halfprism" was used in our experiments with a view to the intensity in the magnifying position (CHRISTIE, Proc. Roy. Soc. 26 (1877) p. 8). Moreover the dispersion is greater in this position, whereas the loss of purity in the spectrum is of no importance here.

[3]) Not too near the critical state the light emitted by the blue mist in a direction normal to the incident light, is polarized in the plane of incidence (RAMSAY, ZS. physik. Chem. 14 (1894) p. 486). It is to be expected that on approach to the critical state the light emitted in the direction mentioned be-

polarisation of $Nic_1$ has been put parallel to that of $Nic_3$. After the tube of ethylene had been brought to the required temperature, and the temperature of the room had been regulated in such a way that the temperature of the tube of ethylene (read to 0°.01) could be kept sufficiently constant (up to some hundredths of a degree) by the addition, when necessary, of some cold or hot water into the vacuum glass, the prism $Nic_2$ was adjusted by rotation so as to obtain equal intensity of the considered portions of the two spectra. With a view to this adjustment care had been taken that the two spectra were as close above each other as possible [1]) and had about the same height. The adjustment and reading were made in the four different positions of $Nic_2$ which gave equality of intensity.

§ 3. *Observations.* Only observations above the critical temperature have been communicated here; in order to get unambiguous data for the dependence of the intensity of the opalescence on the temperature and the density below the critical temperature, a stirring-apparatus, or an arrangement to keep the temperature constant till the thermodynamic equilibrium should have been reached, would have been required. The observations were made after the tube of ethylene had been kept at higher temperature for 15 hours or longer, and had then been slowly cooled down to the temperature of observation. The measurements have been made for two wavelengths, corresponding to $D$ and $F$ in the solar spectrum [2]). In order to give

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comes more and more partially polarized (cf. TYNDALL, Phil. Trans. 160 (1870) p. 348). It would be interesting to examine if then TYNDALL'S residual blue (l. c.) could be observed (on the connection of this with the difference in refractivity of the scattering particles and the surrounding medium see RAYLEIGH, Phil. Mag. (4) 41 (1871) p. 454). Measurements on the condition of polarisation might also lead to an opinion on the size of the particles, see BOCK, Wied. Ann. 68 (1899) p. 674 (spectrophotometrical investigation of the light scattered by a jet of steam, measurement of the condition of polarisation, and determination of the size of the particles by means of diffraction rings) and PERNTER, Denkschr. Kais. Ak. d. Wiss. Wien 73 (1901) p. 301.

[1]) The use of a HÜFNER'S prism would render more accurate adjustments possible.

[2]) When the experiments are repeated under circumstances which admit of a more accurate spectrophotometric adjustment, an extension of the measurements to more wavelengths will be desirable.

an idea of the degree of accuracy of the adjustments, we have communicated in table I the data of an observation at a mean intensity of the scattered light.

TABLE I.

Series VI, No. 3, Nov. 13, 1907.

| Wave length | Temperature | Adjustments of $Nic_2$ | | | | $\Phi$ |
|---|---|---|---|---|---|---|
| $D$ | 11°.69 | 63° 48′ | 36° 36′ | 154° 36′ | 135° 9′ | 14° 10′ |
| | 11 . 66 | 64 24 | 36 15 | 153 30 | 126 18 | 13 50 |
| | 11 . 70 | 63 18 | 36 54 | 154 9 | 125 | 13 53 |
| | 11 . 69 | | | | | — |
| | | temp. mean 11°.68 | | | | mean : 13°58′ |
| $F$ | 11 . 66 | 155° 45′ | 126° 48′ | 65° 18′ | 34° 33′ | 15° 15′.5 |
| | 11 . 68 | 156 15 | 124 54 | 66 9 | 33 54 | 15 54 |
| | 11 . 67 | 157 18 | 122 57 | 67 30 | 34 6 | 16 56 |
| | 11 . 61 | | | | | — |
| | | temp. mean 11°.66 | | | | mean : 16°5′ |

The last column contains the angle of the plane of polarisation of $Nic_2$ derived from the other columns, for the adjustment at equal intensity, with this plane of polarisation when $Nic_2$ crosses $Nic_3$ and $Nic_1$. In general the adjustment for the wavelength $F$ was less accurate than for $D$ on account of the slighter intensity in the spectrum for the former wavelength. The greater deviation which the latter angle $\Phi$ shows for the wavelength $F$ in table I from the preceding ones, may be explained from the difference in temperature.

The results thus obtained have been joined in table II.

TABLE II.

| Wavelength $D$ | | Wavelength $F$ | |
|---|---|---|---|
| Temperature | $\phi$ | Temperature | $\phi$ |
| Series V, Nov. 12, 1907 | | | |
| 13°.53 | 8°27′ | 13°.59 | 10°11′ |
| 12 .55 | 9 45.5 | | |
| Series VI, Nov. 13, 1907 | | | |
| 12°.54 | 10°36′ | 12°.54 | 12°39′ |
| 11 .86$^5$ | 12 37 | 11 .83 | 14 58.5 |
| 11 .68 | 13 58 | 11 .66 | 16 5 |
| 11 .42 | 17 52 | 11 .43 | 18 24 |
| 11 .24 | 22 18 | | |

The observations of series VI ceased after the adjustments for the wavelength $D$ at 11.°24, because after this the temperature fell below the critical temperature, which was determined at 11.°18 [1]) (cf. § 3 beginning).

The difference between the angles $\phi$ for Series V 12.°55 and Series VI 12.°54, wavelength $D$, is owing to this that between these observations a slight modification in the position of the lenses $L_7$, $L_8$ has taken place. The observations mentioned here may serve to bring connection between the series V and VI. The results of other series of observations are not communicated here because for them all the precautions mentioned had not yet been taken.

From the data of table II the course of the intensity of the scattered light with the temperature (§ 2 2$^{nd}$) will be derived in

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[1]) Comparison of this value of the critical temperature with that of other investigators indicates that the critical temperature of the admixture (cf. § 2 p. 16, note 2) does not lie much higher than that of ethylene.

## Errata Communication N⁰. 104*b*.

p. 21 table III: for 11°.61 read 11°.68.

line 6 from the bottom: for "de" read "the".

the first place. Let us call $H_{D,t}$ the intensity in the spectrum of the light scattered by the cloud at the temperature $t$ of the wavelength $D$ for a certain arrangement of the apparatus, which is further thought to be unmodified, $H_{Dcomp}$ the intensity in the comparison spectrum when $Nic_2$ is parallel with $Nic_1$ and $Nic_3$, then $i_{D,t} = H_{D,t}/H_{D,11^{\circ}.68} = sin^4\, \Phi_{D,t}/sin^4\, \Phi_{D,11.^{\circ}68.}$ An investigation of the absolute intensity of the light scattered by the mist compared with that of the incident light (cf. § 6*b*) will have to reveal how to derive a quantity from $i_{D,t}$ which determines the intensity of the scattered light, independent of the particular circumstances of the arrangement. For an examination of the way in which the intensity of the scattered light depends on the temperature, the quantity $i_{D,t}$ is very suitable.

Table III contains the results obtained on this from table II:

TABLE III.

| $t$ | $i_{D,t}$ | $t$ | $i_{D,t}$ |
|---|---|---|---|
| 13°.53 | 0.190 | 11.°6$\overset{8}{1}$ | 1 |
| 12 .54 | 0.337 | 11. 42 | 2.61 |
| 11 .86$^5$ | 0.671 | 11. 24 | 6.11 |

These results have been represented in Pl. II fig. 2, where also a curve has been traced through the points of observation (see further p. 25).

The ratio $r_{F:D,t} = \dfrac{H_{F,t}/H_{F\ comp.}}{H_{D,t}/H_{Dcomp.}} = \dfrac{sin^4\Phi_{F,t}}{sin^4\Phi_{D,t}}$ yields data for the inquiry mentioned in § 2 1st. into the ratio in which the light of different wavelengths is scattered. Table IV contains de results:

TABLE IV.

| $t$ | $r_{F:D,t}$ | $t$ | $r_{F:D,t}$ |
|---|---|---|---|
| 13°.59 | 2.00 | 11°.68 | 1.66 |
| 12 .54 | 2.01 | 11 .43 | 1.18 |
| 11 .56$^5$ | 1.85 | | |

To this purpose the angles $\phi$ for $D$ and $F$ have been reduced to the same temperature by interpolation.

Above 12°.54 the ratio of the intensities of $D$ and $F$ seems to be constant. The fact already observed by several earlier observers that on approach of the critical temperature the mist changes from blue to almost white, is clearly set forth in the table. Measurements on this change of colour, however, have been communicated here for the first time.

§ 4. *On the size of the light-scattering particles* 1) To be able to derive from $r_{F:D}$ the ratio of the intensities $F$ and $D$ of the light scattered in a certain direction by the mist compared with the ratio of the intensities $F$ and $D$ of the incident light on the mist, we must bear in mind: 1st that the two beams of light which are compared with each other in the spectroscope are subjected to different reflections and absorptions outside the spectroscope, which might bring about a change in the ratio of the intensities $D$ and $F$, 2nd that the optical apparatus for observation of the scattered light not being perfectly achromatic might cause a similar change in the ratios of intensities, 3rd that if the condition of polarisation of the two beams is not exactly the same on their arrival in the spectroscope, the reflections in the spectroscope may also give rise to such a change 2).

The influences mentioned under 1 and 2 may be determined and eliminated by measurements of the scattered light when the substance in the neighbourhood of the critical state has been replaced by a suspension for which the ratios of intensities of the scattered light are known 3). Then it will have to appear in how

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1) Cf. § 1 p. 16.

2) Cf. Christie loc. cit.

3) Suspensions for which the intensity of the transmitted light is: according to Rayleigh $I = I_0 e^{-k\lambda^{-4}x}$: mastic, Ag Cl, $Cu_2S$ in water, emulsion of lemon-essence in water: Abney and Festing, Proc. Roy. Soc. 40 (1886) p. 378, Lampa, Wien. Sitz. ber. [2*a*] 100 (1891) p. 730, Hurion, C.R. 112 (1891) p. 1431, Compan, C.R. 128 (1899) p. 1226; according to Clausius $I = I_0 e^{-k\lambda^{-2}x}$: Ba $SO_4$ in a mixture of glycerin and water, etc: Compan loc. cit. To ensure that in this experiment the light is subjected to the same reflections as in the experiments with the mist we should have to take a suspension in ethylene of the critical density.

far the deviation of the values 2 00 found in table IV at the higher temperatures from that which according to RAYLEIGH (Phil Mag. (4) 41 (1871) p. 107) would be found if the scattering were brought about by non-conducting particles the dimensions of which are small with respect to the wavelength : $\lambda^4{}_D/\lambda^4{}_F = 2.129$, is to be explained in this way [1]).

About the influence of what was mentioned under 3 we have made a separate measurement. See for this § 5.

After the corrections indicated in this § have been applied, the data of table IV may serve to give an idea of the size of the particles by the aid of developments such as are given by LORENZ [2]). From the change of $r_{F:D}$ in table IV on approach to the critical temperature may already be deduced that the light-scattering particles must no longer be considered as small with regard to the wavelength at and below 11°.86$^5$ (i.e. 0°.5 above $T_k$).

§ 5. *On the quantity of substance which is condensed in the light-scattering particles at different temperatures* [3]). To get to know the intensity of the scattered light at different temperatures, only a correction has to be applied to table III on account of the circumstance mentioned p. 22 under 3. Therefor the condition of polarisation of the scattered light at different temperatures must first be known (cf. p. 17 note 3). An upper limit for this correction may already be given as follows.

In the measurement mentioned in § 4 (this page) it appeared that light polarized normal to the slit was weakened to a greater degree in the spectroscope than light polarized parallel to the slit, in such a way that the ratio of the intensities in the spectrum is [4]):

$$H_{D\perp}/\ H_D// = 0.82,\quad H_{F\perp}\ /\ H_F\ // = 0.70.$$

If we now suppose that at 13°.53 all the light of wavelength $D$ scattered in a direction normal to the incident light is polarized in the plane of incidence, and that at 11°.24 this light would be totally unpolarized, it follows from this measurement as an upper limit, that at 11°.24 the weakening of the $D$-light in the spectroscope would be 1.10 times the weakening of the $D$-light at 13°.53.

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[1]) Also the fact that the light scattered by the mist must pass through a layer of a certain thickness (± 2 cM.) in the direction of propagation, may cause a deviation in the same direction.

[2]) L. LORENZ. Vidensk. Selsk. Skr. Copenhagen 6 (1890). Oeuvres Scientifiques 1 p. 405.

[3]) Cf. § 1 p. 16.

[4]) Cf. with this the calculations of CHRISTIE Proc. Roy. Soc. 26 (1877) p. 24.

To be able to derive from the intensity of the scattered light at different temperatures how the quantity of condensed substance depends on the temperature, we should have to get a somewhat complete insight into the way in which the light is scattered by such particles, and hence be acquainted with the structure of the particles (cf. § 1), in which also the origin (cf. Comm. N°. 104$a$, § 4) would come in for discussion. However, it is to be expected that when the particles are small compared with the wavelength of the light, the intensity of the scattered light will increase proportional to the square of the quantity of condensed substance, whereas when the particles are no longer so small, the increase will take place more slowly.

To whatever cause we may attribute the occurrence of the differences in density, the great compressibility of the substance in the neighbourhood of the critical state will have a preponderating influence on it. Thus e.g. the mean deviation in density governed by the statistic equilibrium (Smoluchowski)[1] will be proportional to $\sqrt{\partial p/\partial \rho}$ ($\rho =$ density). If we assume that the substance condenses round centres of attraction which exert forces on the surrounding particles of the substance which per unit of mass are only dependent on the distance, the quantity which is condensed round every centrum of attraction is proportional to[2] $\partial p/\partial \rho$.

In order to examine what information the data in table III give on a connection between the intensity of the scattered light and the compressibility, we notice that in the neighbourhood of the critical point $\partial p/\partial \rho = q_{11} (T - T_k)$, if the average density of the substance differs so little from $\rho_k$ that the following term $3q_{30} (\rho - \rho_k)^2$ may be neglected (so $T - T_k$ not too small).

In table V the data of table III have been compared with the formula: $i_{D,t} = \dfrac{0.5}{T - T_k}$ ($t_k = 11°.18$, see p. 20).

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[1] M. v. Smoluchowski, Ann. d. Phys. (4) 25 1908 p. 206.

[2] In this it is supposed that the condensation is so insignificant that $\rho$ in a condensed part remains sufficiently near $\rho_k$.

TABLE V.

| $t$ | $i_{DtO}$ | $i_{DtC}$ | O—C in % of O |
|---|---|---|---|
| 13.°53 | 0.190 | 0.213 | — 12 |
| 12.54 | 0.337 | 0.368 | — 9 |
| 11.86⁵ | 0.671 | 0.730 | — 9 |
| 11.68 | 1 | 1 | |
| 11.42 | 2.61 | 2.08 | + 20 |
| 11.24 | 6.11 | 8.33 | — 36 |

The — — — — curve in Pl. II fig. 2 represents $i_{DtC}$.

The differences O — C are of two kinds:

1. The deviation at 11°.24: this was to be expected in the immediate neighbourhood of the critical temperature, as the formula for $T_k$ would give an infinite intensity; here the influence makes itself felt of following terms in the development of $\partial p/\partial \rho$, or of the intensity of the scattered light as function of the quantity of substance (see p. 24);

2. also at temperatures further from the critical temperature there is a systematic deviation: the observed curve of intensity ascends here more rapidly than the calculated one. This might among others be in connection with the observation of TRAVERS and USHER [1]) who found that the maximum of the intensity of the opalescence should not lie at $T_k$ but for $SO_2$ 0°.05 above $T_k$.

Leaving these deviations out of account we may conclude that on the main the observations conform to the mentioned equation. The deviations from a formula $i_{D,t} = \frac{0.25}{(T-T_k)^2}$ would have been much larger. The correction mentioned in the beginning of this § will not affect this conclusion.

On the supposition that at least when the dimensions of the volume elements in which appreciable condensations or rarefactions are found, are small with respect to the wavelength, the intensity of the scattered light is proportional to the square of the quantity of substance which has condensed round every centrum, or to the square of the mean deviation in density governed by the statistic equilibrium it follows that our observations rather support the hypothesis of the condensations and the rarefactions caused by the molecular movement and governed by the statistic equilibrium, than the hypothesis of centres of attraction whose number remains constant with varying temperature.

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[1]) M. W. TRAVERS and F. L. USHER. Proc. Roy. Soc. A. 78 (1906) p 247.

If it appears from further investigations that the absolute value of the intensity of the light scattered by the mist is in harmony with what is to be expected according to the distribution law of BOLTZMANN (cf. SMOLUCHOWSKI, loc. cit.) a connection may be formed between the observations of the intensity of the light scattered by the mist and the disturbance function in the equation of state in the neighbourhood of the critical point through considerations on the increase of the virial of attraction in consequence of the differences of density [1]).

§ 6. *Remarks on further experiments on the mist in the neighbourhood of the critical state.*

*a.* When through measurements as treated in § 3 the way in which the intensity of the light scattered by the mist depends on temperature and density, will have been sufficiently brought to light, the determination of this intensity at different heights in a CAGNIARD-LATOUR tube may be substituted for the method of the floating bulbs for the determination of the density at different heights in the tube (See Comm. N⁰. 98). If the establishing of the thermodynamic equilibrium is effected by keeping the temperature for a long time sufficiently constant, the determination of the intensity of the scattered light as function of the height in the tube would supply a method for the accurate determination of the experimental equation of state in the immediate neighbourhood of the critical state (cf. Comm. N⁰. 98 § 1 p. 6).

*b.* Besides the before-mentioned measurements on the condition of polarisation (§ 2) and the measurements for the sake of the corrections mentioned in § 4, measurements on the ratio between the intensity of the scattered light and that of the incident light would also be desirable (cf. § 3 p. 21 and § 5 p. 26). For this purpose measurements might serve in which the ethylene is replaced by a silver mirror forming an angle of 45° with the axis of the tube [1]).

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[1]) Cf. M. v. SMOLUCHOWSKI, BOLTZMANN Festschrift 1904, p. 626.

*c.* It would be of interest to investigate whether for a single substance in the neighbourhood of the critical point an increase of viscosity is found as has been noted by OSTWALD [2]) for a liquid mixture in the neighbourhood of the critical point of separation from measurements of STEBUTT, and has been further determined by FRIEDLÄNDER (see p. 15). Perhaps the increase of the viscosity and the size of the light-scattering particles (§ 1) might be brought into relation, and so also the colour of the scattered light.

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[1]) We have in the meantime made a preliminary measurement of the absolute intensity of the scattered light by comparing it with the light reflected from a silver mirror (reflection constants for light polarized perpendicular and parallel to the plane of incidence calculated according to QUINCKE, Pogg. Ann. 128 (1866) p. 541 from determinations of the principal angle of incidence and the principal azimuth by JAMIN, Ann. chim. phys. (3) 22 (1848) p. 311). For this measurement the comparison spectrum had to be intensified by replacing the systems of lenses $L_7$ and $L_8$ by stronger combinations. From the angles $\phi_{Ag} = 31°33'$ and $\phi_{Et} = 5°4.'5$ we derive that at $t = 11°.93$ the quantity of the light of wavelength $D$ scattered by 1 cM.$^3$ of ethylene perpendicular to the direction of incidence per unit angle of vision is $s_D = 0.0007$, if the quantity of the incident (unpolarized) light $= 1$.

If we calculate according to RAYLEIGH, Phil. Mag. (5) 12 (1881) p. 86—88, LORENZ, Oeuvres Scientif. I p. 496, $s = \frac{2\pi^2}{N\lambda^4} \frac{(\Delta\mu)^2}{{\mu_0}^2}$ ($N$=number of light-scattering particles per cM$^3$, $\Delta\mu$ deviation from the average refractive index $\mu_0$). and if we express $\Delta\mu$ in terms of the deviation in density according to LORENTZ-LORENZ, and if according to SMOLUCHOWSKI we write $\overline{\delta^2} = - R\, T_0 / \nu\, {v_0}^2 \left(\frac{\partial p}{\partial v}\right)_0$ ($\nu$ = number of molecules in the light-scattering particle) in which $\left(\frac{\partial p}{\partial v}\right)_0$ for $v_0 = v_k$ can be developed as $\frac{p_0}{v_0\, T_0}\, \mathfrak{p}_{11}\, (T - T_k)$ (Suppl. N°. 6), we find at $T - T_k = 0.75$ for $s_D = 0.00075$.

Although our measurement is but preliminary, it leads us to conclude from the agreement of the observed value with the value calculated above that, at least as far as the order of magnitude is concerned, the intensity of the light scattered by the blue mist in a single substance in the neighbourhood of the critical state agrees with the hypothesis of SMOLUCHOWSKI, that that light is due to differences in density caused by molecular motion and governed by statistic equilibrium.

[2]) W. OSTWALD. Lehrbuch der allgemeinen Chemie II 2 (2te Aufl.) p. 684.

*d.* We could not ascertain an influence of RÖNTGEN-rays on the blue mist in ethylene. An investigation might be made as to whether the $\alpha$-rays or the emanation of radium exert an influence on the mist.

*e.* FÜCHTBAUER [1]) investigated a mixture of iso-butyric acid and water in the neighbourhood of the critical point of separation ultramicroscopically; he did not succeed in dissolving the cone of light. Nor could we ascertain [2]) the presence of separate light-scattering particles in the mist for a mixture of amylene-aniline with the objective Homog. Imm. $\frac{1}{12}$ [3]), eye-piece 4, condenser *AA* (ZEISS) and as source of light an electric arc lamp (30 Ampère) or solar light (10 Dec. '07). We consider a repetition of this experiment with more intense solar light and with more precautions taken to keep the mixture that is ultramicroscopically examined, at a constant temperature near the critical temperature of separation, desirable, and also such an investigation for a single substance in the neighbourhood of the critical point gas-liquid [4]).

This investigation in connection with what follows (see § 4) from measurements as mentioned in § 3 on the size of the light-scattering particles might give us an idea of the velocity of motion of the light-scattering particles or of the mean time of existence of definite aggregations governed by the statistic equilibrium.

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[1]) CHR. FÜCHTBAUER, ZS. physik. Chem. 48 (1904) p. 552.

[2]) We express our hearty thanks to Prof. M. DE HAAS of Delft for his kindness to lend us his ultramicroscopic apparatus.

[3]) A water immersion objective of great aperture was not at our disposal.

[4]) The possibility is namely not excluded that then the light-scattering particles have larger dimensions and a greater mutual distance than at the critical point of separation of two liquids. To form an opinion on this point a spectrophotometric investigation for a liquid mixture, in the same way as we have made for a single substance (§ 3) would be useful.

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

## No. 105.

**Dr. H. KAMERLINGH ONNES**. "Experiments on the condensation of helium by expansion.

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam*, **28 Maart 1908**, p. 744—747).

EDUARD IJDO — PRINTER — LEIDEN.

**Dr H. KAMERLINGH ONNES**. "*Experiments on the condensation of helium by expansion.*" [1])

In the last session I communicated what I had observed in expanding helium, which at a temperature of — 259° C. had been strongly compressed. I made the experiment in consequence of my determinations of the isotherms of helium at different temperatures i. a. also at — 253° C. and — 259° C., from which I had calculated about 5° K. for the critical temperature of helium [2]). It thence followed that it would be possible by rapid expansion of helium compressed at 100 atm. at the meltingpoint of hydrogen to pass below the critical temperature and to cause a mist to appear in the gas [3]). It was to put this conclusion to the test, that I compressed nearly 7 liters of helium, purified by burning with copperoxyde and leading over charcoal at the temperature of liquid hydrogen (so that I could trust to have a gas with only very small admixtures) in a thick-walled tube placed in a not silvered vacuumglass with liquid hydrogen, and provided with a stopcock through which the helium could be let off from the tube into a gasholder, a gasbag or a vacuum. The liquid hydrogen round the tube was exhausted at such a pressure that hydrogen crystals just appeared at the surface of the liquid. The vacuumglass with hydrogen was surrounded by a second not silvered vacuumglass with liquid air. In the thick-walled tube, leaving only a small clearance, there was placed an extremely thin-walled beaker [1]) for protecting the gas which was cooled by expansion against conduction of heat from the walls, the layer of gas between the beaker and the walls of the tube, though it was very thin, being a bad conductor.

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[1]) The content of this Communication is the same as that of a letter to the Editor of Nature, Apr. 23 1908, where I drew also attention to the fact that as recently as the year before in an address to the Dutch Congress of Natural Science and Medicine (see Comm. Suppl. No. 18*a*) I had expressed the opinion that it would be scarcely possible to liquefy helium, OLSZEWSKI and DEWAR having not succeeded in liquefying it by expansion and some experiences of my own on the sinking of helium in liquid hydrogen seeming to indicate that helium was nearly a perfect gas. At the same meeting I indicated the determination of the isothermals of helium as the direct way to the calculation of the critical temperature. The first results I obtained in this way changed completely my views on the liquefaction of helium.

[2]) OLSZEWSKI from expansion experiments had deduced that the critical temperature of helium lies below 2° K. DEWAR estimates the *boiling* point according to the absorption in charcoal at higher than 5° K. (This would agree with a critical temperature of 8° K.)

[3]) Liquefaction by making use of the JOULE-KELVIN process would also be possible.

At the expansion of the helium a dense gray cloud appeared from which separated out solid masses floating in the gaseous helium, resembling partly cotton wool, partly also denser masses, as if floating in a syrupy liquid, adhering to the walls and sliding downward while at the same time vanishing rapidly (20″). There was no trace of melting.

As far as I could judge then from the experiments I considered it probable that this solid substance was for the greater part helium.

If helium passed immediately to the solid state then the position of the vapour line in respect to the adiabatics would be more favourable for condensation than was to be expected according to the formula of VAN DER WAALS. The voluminous aspect of the solid mass was in harmony with this. By the above and also by other observations which afterwards gave rise to doubt or proved incorrect, I had for some time the conviction that I had seen solid helium rapidly giving off vapours of the pressure shown by the gas (once more than 15 atm. was observed).

The continuation of my experiments has shown that they must be explained in quite a different way. By a not sufficiently explained cause the gas proved to be not so pure as was to be expected considering the method of purification. In analyzing what was absorbed by charcoal at the temperature of boiling hydrogen till the charcoal did no more absorb hydrogen (so that the gas could only contain traces of hydrogen), it could be proved that in one case the gas has contained only 0.45 and in another only 0.37 volume percents of hydrogen at most [1]) But this small admixture must have had a very great influence.

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[1]) This device has been used by OLSZEWSKI in his experiments on the expansion of hydrogen.

For at a repetition of the experiment with the helium subjected to the new treatment no cloud at all was observed. The experiment is not decisive as the velocity of expansion had been too small, but it is difficult before further investigation to find in the difference of velocity of expansion the cause that the helium in the tube remained now perfectly clear.

The explication of the previous observations is to be found in solution phenomena of solid hydrogen in gaseous helium. The phenomena which made the impression of being the giving off of vapour had been the solution of deposited solid hydrogen in the gaseous helium, the latter rapidly returning from the lower temperature to that of melting hydrogen, and the pressure increasing in consequence. Helium at the temperatures, that come into account here can according to the theory of mixtures take up at every temperature a percentage of hydrogen determined by that temperature in such a way that it is not deposited at any pressure. On plausible suppositions one can deduce that at temperatures above the melting point of hydrogen this percentage can be considerable and that at this melting point itself it can be more than one percent. From mixtures with smaller percentage the hydrogen is only deposited at lower temperatures e.g. by expansion. By the smallness of the quantity of hydrogen present it is also explained that after prolonged blowing off of the helium no solid hydrogen was left. For the quantity left was so small that it could evaporate in the space which it found at its disposal.

It remains remarkable that as small a quantity of admixture as the gas contained has been able to give the total phenomenon of a substance condensing to a solid and evaporating again, though the rapid evaporation, in which even denser masses were seen to be blown away sometimes, is in harmony with the smallness of this quantity of substance. There cannot have been much more in the tube than in round numbers 1 mgr. or 15 cubic millimetres of hydrogen — probably there was less in it — and yet the tube of nearly 7 cubic centimetres was over its whole length for almost a quarter filled with a dense flaky substance.

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[1]) About a small possible quantity of neon I could not yet be certain.

As far as the experiments on the expansion of helium at the melting point of hydrogen are now advanced they show the curious forms that the solution phenomena of a solid in a gas take in the case of helium and hydrogen. They further point to the possibility of realizing with mixtures of hydrogen and helium the rising or falling of the solid substance according to the pressure exerted on the gas, the barotropic phenomenon for a solid and a gas. But the question of condensing helium is to be considered yet as an open one, which will ask an extensive investigation.

## POSTSCRIPTUM.

I have had the occasion to repeat the experiment with the gas that remained perfectly clear in the last expansion experiment; and which also according to the spectroscopic test contained only traces of hydrogen. I now used a greater velocity of expansion. A thin cloud appeared and vanished extremely rapidly (in 1″ nearly) The mist now had another aspect.

It is possible that the traces of hydrogen left in the gas will prove sufficient to cause this mist. But it is also possible that the mist has been a liquid cloud and the changed aspect seemed to point to this. If this might prove to be the case then the critical point would be nearly as I calculated it from the isothermals and helium would follow tolerably well the laws of VAN DER WAALS. The tube broke and I could not attain more certainty about the nature of the cloud.

The preceding experiments show very strikingly how careful one has to be in making conclusions from the appearing or not appearing of a cloud by expansion. A decision about the critical temperature of helium is therefore only to be obtained by a prolonged systematical investigation which will take much time.

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PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

## No. 106.

**Dr. H. KAMERLINGH ONNES and Dr. C. BRAAK.**
"Isotherms of diatomic gases and their binary mixtures. VIII. The breaking stress of glass and the use of glass tubes in measurements under high pressure at ordinary and low temperatures." (*With a plate*).

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam,* **24 April 1908,** p. 890—897.)

Eduard IJdo — Printer — Leiden.

**Dr. H. KAMERLINGH ONNES and Dr. C. BRAAK. "Isotherms of diatomic gases and their binary mixtures. VIII. The breaking stress of glass and the use of glass tubes in measurements under high pressure at ordinary and low temperatures."**

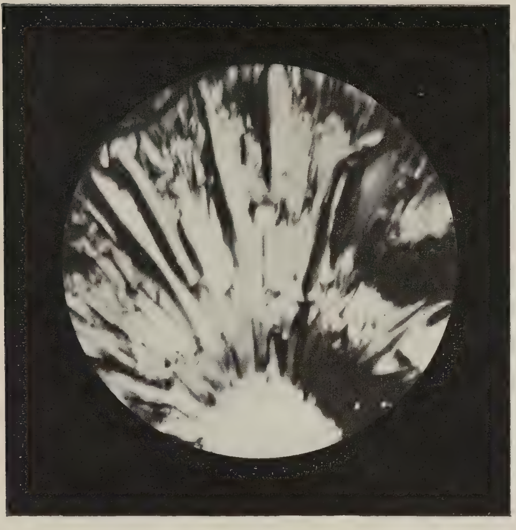

Fig. 1.

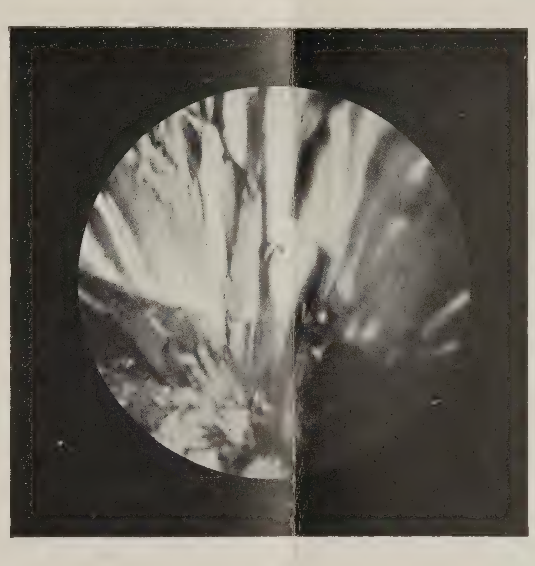

Fig. 2.

Communication N°. 106.

**Dr. H. KAMERLINGH ONNES and Dr. C. BRAAK.** — „*Isotherms of diatomic gases and their binary mixtures* VIII. *The breaking stress of glass and the use of glass tubes in measurements under high pressure at ordinary and low temperatures*".

§ 1. *Introduction.*

With former determinations of isotherms (Comms. N$^{os}$. 78, 97*a*, 99*a*, 100*a* and 100*b*, 102*a* and 102*b*) we could not raise the pressure above 60 atm. For in order to reach the required accuracy of about $^1/_{2000}$ we want a manometer which is reliable to the same degree. And till now we could only reach this degree of accuracy by means of a calibration with the open manometer described in Comm. N$^0$. 44 (Nov 1898) which reads to 60 atm. only. Already long ago we intended to include the higher pressures in our investigation. As a first step in that direction we have raised the upper limit of the pressure to 120 atmospheres. For while keeping the same arrangement we could easily complete the existing open manometer to one of the same accuracy reading to 120 atmospheres by merely adding a number of new manometer tubes of greater resisting power than those we had.

The new manometer and also the other apparatus intended for pressures to 120 atmospheres are nearly completed and will soon enable us to determine the isotherms to 120 atm. Afterwards we hope that these will be followed by measurements at still higher pressures. It seems even possible to reach 500 atmospheres with almost the same accuracy.

For all these investigations it is a great advantage when the piezometer and manometer tubes can be made of glass.

Therefore we have investigated in how far this would be possible with regard to the breaking stress of glass.

The breaking stress of glass has been investigated most at ordinary temperature, because it is in the first place desirable that the reservoirs of the manometer tubes of the open manometer and the divided stems of the piezometer tubes should be made of glass.

To these measurements we have added a series of determinations at lower temperatures in order to judge to what extent glass piezometer reservoirs could be used for the higher pressures at these temperatures.

Investigations on the maximum strain of glass have been made by GALITZIN [1]) and by WINKELMANN and SCHOTT [2]). The former has determined the inner pressure which cylindrical glass tubes can resist, the latter two have determined the maximum strain of glass rods. GALITZIN's determinations, however, were made only at relatively small pressures [3]), those of WINKELMANN and SCHOTT only at ordinary temperature.

In our investigation we partly follow the method of GALITZIN. From the theory of elasticity we can derive in connection with the dimensions of the apparatus the maximum tension in the glass from the maximum pressure which the glass tube resists. The results obtained in this way were compared with the direct data obtained in a second series of measurements, where the maximum strain of glass rods was determined. If we take into consideration the material investigated, it is not astonishing that the results of the two series show irregular differences. These differences however are of no influence upon some general conclusions that may be drawn from the measurements.

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[1]) Bull. de l'Acad. Imp. des Sciences de St. Pétersbourg, V$^e$ Serie, B. XVI N$^0$. 1.

[2]) Wied. Ann. 51 (1894) p. 697.

[3]) So also the late measurements of BRADLEY and BROWNE, Journ. phys. chem. 8 (1904) p. 37, which we regret to have overlooked in our original paper. For quotations of previous researches we refer to WINKELMANN and SCHOTT l. c.

### § 2. *Determinations at ordinary temperature.*

*Survey of the observations and arrangement of the measuring apparatus.*

1. *Determination of the maximum inner pressure.*

The experiments were made with ordinary Thüringer glass. A cylindrical reservoir of the glass to be investigated was fused on to a thick-walled glass capillary. The capillary was provided at its end with a steel nut with a hexagonal part by means of which it could be screwed on to a steel capillary which is connected to a pressure pump with a metal manometer. For measurements to 200 atms. it was fixed on the glass by means of sealing wax, for higher pressures it was soldered to the glass (comp. Comm. N$^0$. 99*a* § 15). If carefully made this connection proved able to resist the highest pressures (1200 atms.) The tubes were previously annealed carefully.

According to their dimensions they can be divided into three kinds:

*a.* thick-walled tubes with large inner bore.

*b.* thick-walled capillaries

*c.* thin-walled tubes with large inner bore.

It will appear that these three kinds of tubes give results different for each group

The accuracy of the manometer is about $2^0/_0$ which is quite sufficient for our purpose.

2. *Direct measurement of the maximum strain $T_m$ by the determination of the breaking stress.*

In order to prevent as much as possible unequal strain during the suspension we have used here glass threads of at the most 0.6 mm. thickness [1]).

In order to reduce the tensions to minimum the glass rod was bent to a hook at either end. It was then suspended by the upper hook and the rod was drawn out in the middle to a thread by applying a certain force to the lower hook in about the same way as in the actual experiment. The weight used was a beaker into which water flowed.

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[1]) In the experiments of Winkelmann and Schott where thicker rods of 10—20 mM$^2$. section were used this required great care.

§ 3. *Results.*

1. *Determinations with cylindrical tubes and internal pressure.*

In order to facilitate a comparison with GALITZIN's results we take the same value $\frac{1}{4}$ for the coefficient of contraction. Let $P_m$ be the maximum internal pressure, $2R$ the external diameter, $2R'$ the inner diameter (this is further on expressed in mm), and let $n = \frac{R}{R'}$, then we can represent the maximum tension $T_m$ in the glass (in this case that of the internal portions of the glass in a direction perpendicular to the axis of the cylinder) by:

$$T_m = \frac{1}{4}\left\{5\,P_m + 7\left(\frac{P_m - 1}{n^2 - 1} - 1\right)\right\}.$$

If, as is the case in the following tables, $P_m$ is expressed in atmospheres, we find $T_m$ expressed in KG/mm$^2$ (as it is given in the following tables) by multiplying the value found above by 0.01033.

For the three series mentioned in § 2 sub *a*, *b* and *c* the results have been combined in the table below. The meaning of the columns will be clear after what has just been said. Where several results are given under one number we have after the tube had partly burst (for instance so that only the end had broken off, or the tube had broken near the steel piece) used the same tube again for the following experiment.

The results for $T_m$ are lowest for series *a* and highest for series *b*. In the latter series this is especially the case for the tubes with a very small inner bore if we except nos. 12 and 13 where the soldering was ineffective. Helped by the experience made we have treated the following tubes more carefully. With the tubes which have burst under a too low pressure the existence of irregular tensions appears clearly from the way of bursting, where the break has a transverse or irregular direction and not, as theory requires, parallel to the axis.

## TABLE I.

Maximum internal pressure and tension of cylindrical glass tubes.

| N$^0$ | $2R$ | $2R'$ | $n$ | $P_m$ | $T_m$ |
|---|---|---|---|---|---|
| Series *a* | | | | | |
| 1 | 9.3 | 3.5 | 2.66 | 340 | 5.38 |
| 2 | 8.8 | 4.0 | 2.20 | 280 | 4.91 |
| 3 | 8.7 | 4.2 | 2.07 | 230 | 4.21 |
| 4 | 9.4 | 3.2 | 2.94 | 270 | 4.10 |
| 5 | 9.2 | 3.0 | 3.07 | 380 | 5.70 |
| 6 | 9.7 | 4.2 | 2.31 | 370 | 6.30 |
| 7 | 10.4 | 4.0 | 2.60 | 240 | 3.83 |
| 8 | 12.8 | 5.8 | 2.21 | 260 | 4.54 |
| 9 | 17.6 | 5.0 | 3.52 | 290 | 4.19 |
| Series *b* | | | | | |
| 10 | 7.4 | 1.00 | 7.40 | 510 | 6.74 |
| 11 | 6.8 | 1.00 | 6.80 | 420 | 5.57 |
| 12 | 7.5 | 0.27 | 27.78 | 460 | 5.93 |
| 13 | 6.5 | 0.35 | 18.57 | 500 | 6.46 |
| 14 | 6.7 | 0.24 | 27.92 | 540 | 6.97 |
| | | | | 800 | 10.33 |
| | | | | 1100 | 14.21 |
| 15 | 6.7 | 1.08 | 6.20 | 530 | 7.08 |
| 16 | 5.9 | 0.70 | 8.43 | 680 | 8.94 |
| 17 | 5.8 | 0.46 | 12.61 | 1200 | 15.61 |
| 18 | 5.9 | 0.62 | 9.52 | 820 | 10.74 |
| 19 | 5.3 | 0.46 | 11.52 | 920 | 11.99 |
| 20 | 5.5 | 0.46 | 11.96 | 1060 | 13.80 |
| 21 | 6.6 | 1.00 | 6.60 | 660 | 8.78 |
| 22 | 7.2 | 1.40 | 5.14 | 520 | 7.07 |
| 23 | 6.4 | 1.35 | 4.74 | 520 | 7.13 |
| Series *c* | | | | | |
| 24 | 3.8 | 2.42 | 1.57 | 283 | 7.12 |
| 25 | 5.6 | 4.00 | 1.40 | 193 | 6.09 |
| 26 | 6.4 | 4.78 | 1.34 | 221 | 7.84 |
| 27 | 6.9 | 3.91 | 1.76 | 329 | 7.06 |
| 28 | 7.4 | 5.11 | 1.45 | 179 | 5.21 |
| 29 | 7.9 | 5.46 | 1.45 | 157 | 4.57 |
| 30 | 3.5 | 2.26 | 1.54 | 261 | 6.78 |
| 31 | 6.8 | 5.13 | 1.32 | 203 | 7.52 |
| 32 | 7.4 | 5.19 | 1.43 | 201 | 6.04 |
| 33 | 6.8 | 5.78 | 1.18 | 66 | 3.83 |
| 34 | 3.8 | 2.42 | 1.57 | 377 | 9.49 |
| 35 | 3.8 | 2.50 | 1.52 | 277 | 7.36 |
| 36 | 6.0 | 4.37 | 1.37 | 179 | 5.96 |
| 37 | 6.8 | 5.17 | 1.31 | 159 | 6.02 |
| 38 | 6.8 | 4.85 | 1.40 | 169 | 5.33 |
| 39 | 7.3 | 5.62 | 1.30 | 109 | 4.22 |
| 40 | 7·8 | 7.31 | 1.067 | 54 | 7.60 |

2. *Maximum strain of glass threads.*

The diameter of the threads lies between 0.1 and 0.6 mm. The results are combined in the two following tables. The bore was determined by a measurement of the diameter in two directions at right angles. The mean of these two measurements is given in the tables. The first table contains the results obtained with glass threads which have undergone only the operation mentioned sub § 2. To investigate the influence of irregularities which thus may remain in the structure of the glass we have made a series of measurements by means of threads which had beforehand been heated to incandescence and then cooled very slowly. The results of this series are combined in table III.

TABLE II.

Maximum strain of unannealed glass threads.

| Stress in grams | Diameter in mm | $T_m$ in KG/mm². | Stress in grams | Diameter in mm. | $T_m$ in KG/mm². |
|---|---|---|---|---|---|
| 257.6 | 0.119 | 23.1 | 2615 | 0.424 | 18.4 |
| 496.5 | 0.192 | 17.5 | 2785 | 0.446 | 17.8 |
| 457.8 | 0.159 | 22.9 | 1425 | 0.351 | 14.7 |
| 2325 | 0.384 | 19.8 | 1635 | 0.370 | 17.5 |
| 1175 | 0.257 | 22.7 | 1325 | 0.325 | 16.0 |
| 1475 | 0 325 | 17.6 | 1555 | 0.298 | 22.4 |
| 1695 | 0.311 | 22.4 | 2335 | 0.370 | 21.5 |
| 4105 | 0.487 | 22.1 | | | |

Except the thread for which $T_m$ is lowest viz. 14.7 all the threads of table II show where broken a sharply ridged structure while we find at the edge a small semicircular smooth spot as was found by Winkelmann and Schott [1]).

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[1]) p. 718 loc. cit.

With regard to the series of table III we may remark the following. In order to prevent changes of form of the threads suspended in the furnace and softened by the heat under the influence of gravitation, which afterwards during the measurements might give rise to irregular tensions, we have shaped the extremities (cf. § 2) not into hooks as in the former series but to closed rings in such a way that the whole becomes as symmetrical as possible with regard to a plane through the longitudinal axis. A comparison of the tables II and III shows that the two methods lead to the same results.

## TABLE III.

Maximum strain of annealed glass threads.

| Stress in grams | Diameter in mm. | $T_m$ in KG/mm$^2$. | Stress in grams | Diameter in mm. | $T_m$ in KG/mm$^2$. |
|---|---|---|---|---|---|
| 2920 | 0.438 | 19.4 | 1940 | 0.325 | 23.4 |
| 3530 | 0.597 | 12.6 | 1760 | 0.322 | 21.6 |
| 2120 | 0.532 | 9.5 | 2850 | 0.445 | 18.3 |

Of the glass thread with the lowest $T_m$ (cf. table III) the section was little ridged but smooth, to the next value of $T_m$ (= 12.6) belonged a relatively large smooth semicircular spot, while for the highest $T_m$ (= 23.4) no spot was to be seen, but the whole section showed a very sharply ridged structure. All these facts agree with what has been found by WINKELMANN and SCHOTT[1]).

On the plate we show the structure of the sections of a couple of threads at the place where the thread has broken. They both clearly show the smooth parts and the structure radiating thence. The smallest diameter of the sections is 0.530 and 0.555 mm. respectively.

---

[1]) loc. cit.

## § 4. *Conclusions.*

Table I shows that as to the series $a$ and $c$ our results agree tolerably well with those of Galitzin [1]).

Those of the series $b$, however, show that the result derived by him for the maximum internal pressure, viz. 623 atms. is too low, because the highest pressure observed by us is 1200 atms. For the tubes of the series $b$ $T_m$ appears to lie higher than would be expected from the observations in the two other series. Probably this must be explained as follows. From a comparison between the 3 series it appears that series $a$ gives the lowest results for $T_m$, series $b$ the highest. The fact that the values for $a$ are lower than for $c$, must probably be ascribed to the circumstance that with almost equal internal bores the wall is thickest for the first series and hence the chance of abnormal stresses is greater. For series $b$ the wall is thicker than for $c$, but the inner bore is much smaller, and hence the existence of inequalities and scratches on the surface which unfavourably influence the breaking stress [2]) are reduced to a minimum. For the tubes for which $2R' = 1$ mm. it seems that the two factors neutralize each other, for those with the smaller inner bore the favourable influence of the surface being smaller preponderates.

In order to investigate in detail in how far the above mentioned two unfavourable factors influence $T_m$ we have applied the direct determination with thin glass threads of which the surface is as smooth as possible and where owing to the small bore abnormal tensions are necessarily small. The results which are much higher than those of Winkelmann and Schott, agree with those found by means of the first method and seem to justify the supposition made above about the unfavourable influence of a not perfectly smooth surface and inner abnormal stresses. They point to an upper limit for $P_m = 1700$ atms.

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[1]) Table I p. 12 and 13, loc. cit.

[2]) Cf. Winkelmann and Schott, loc. cit.

## § 5 *Determinations at low temperatures.*

The determinations in liquid air were made in the same way as those at ordinary temperature. The lower hook of the glass thread was fastened to a wooden bearer, placed beside the thread in a vacuum glass with liquid air.

The first determinations gave results which differed much from the later ones. Their mutual agreement is very bad and they are characterized by very high values for the maximum strain, which vary from 44 to 73 KG. per mm$^2$. while for the ordinary temperature the highest strain was 23 KG. per mm$^2$. Also the structure of the section was totally different, being scarcely ridged but smooth. The smooth spot on the section was as a rule missing. In these measurements the threads were pulled asunder almost immediately after they had been placed in liquid air. Before the following measurements they were left at least 20 minutes in the bath of low temperatures. The latter gave lower results with a better mutual agreement. The structure of the section is similar to that at ordinary temperature, generally a little less distinct. The results are combined in the following table.

### TABLE IV.

Maximum strain of glass threads at the temperature of liquid air.

| Stress in grams | Diameter in mm. | $T_m$ in KG/mm$^2$. | Stress in grams | Diameter in mm. | $T_m$ in KG/mm$^2$. |
|---|---|---|---|---|---|
| 1993 | 0.280 | 32.4 | 2498 | 0.297 | 35.9 |
| 2653 | 0.372 | 24.3 | 2055 | 0.286 | 31.9 |
| 2523 | 0.290 | 38.2 | 3550 | 0.359 | 35.1 |
| 1293 | 0.236 | 29.5 | 3865 | 0.396 | 31.3 |

The results are still much higher than for the ordinary temperature, a very favourable result for measurements at low temperature.

Lastly a single determination in liquid hydrogen was made. Fifteen minutes after the thread had adopted the temperature of the bath it was pulled asunder. The total weight was 3013 grams, the diameter 0.271 m.m., hence the maximum strain in KG/mm$^2$. = 52.1, again much higher than at the temperature of liquid air. The structure of the section was striated, unridged and no smooth part occurred.

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# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

OF THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,
*Director of the Laboratory.*

## No. 107a.

**Dr. H. KAMERLINGH ONNES** and **Dr. C. BRAAK**. "On the measurement of very low temperatures. XXI. On the standardizing of temperatures by means of boiling points of pure substances. The determination of the vapour pressure of oxygen at three temperatures". (*With a plate*)

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam*, **30 Mei 1908**, p. 86—93).

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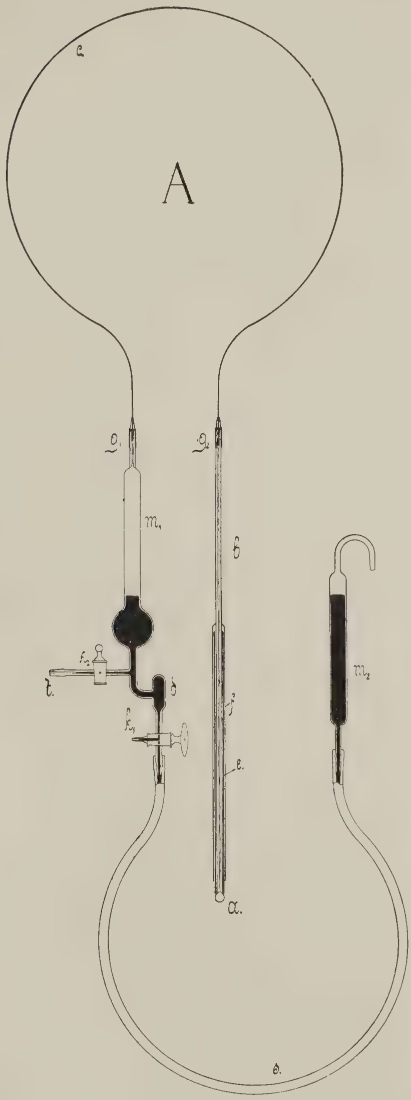
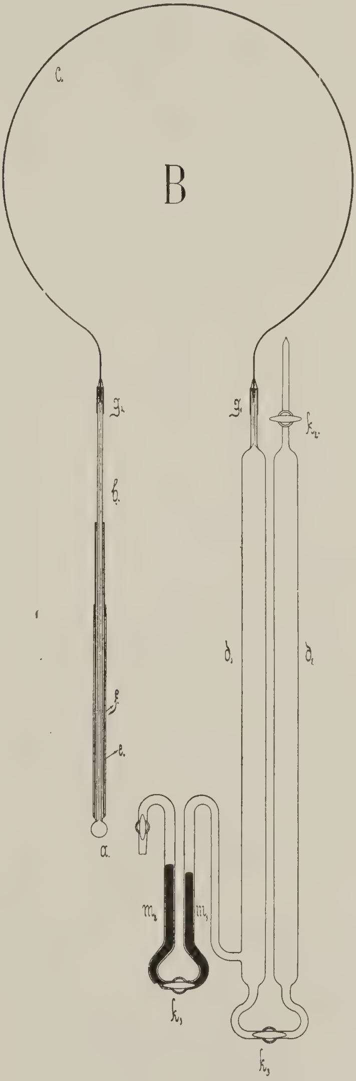
Dr. H. KAMERLINGH ONNES and Dr. C. BRAAK. "On the measurement of very low temperatures. XXI. On the standardizing of temperatures by means of boiling points of pure substances. The determination of the vapour pressure of oxygen at three temperatures."

PLATE I.





Communication No. 107^a.

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## **Dr. H. KAMERLINGH ONNES and Dr. C. BRAAK.** "*On the measurement of very low temperatures.* XXI. *On the standardizing of temperatures by means of boiling points of pure substances. The determination of the vapour pressure of oxygen at three temperatures.*"

§ 1. *Introduction.* In a preceding Communication (N$^0$. 101*a*) we have spoken of the desirability of determining once for all certain temperatures by means of boiling point apparatus, because the points of the temperature scale thus fixed have the advantage over those fixed with resistance thermometers and thermoelements that they do not depend on the durability of special apparatus and they facilitate comparisons between thermometers in different laboratories.

This Communication treats of a number of determinations with oxygen: *a.* a little above and a little below the normal boiling point from which the latter could be derived; *b.* at 366 and 516 mm. mercury pressure which may serve to give information about the further course of the vapour pressure curve.

After some preliminary determinations we have constructed two apparatus of different dimensions, in each of which different quantities of gas could be successively condensed. Thus we have obtained two series of independent determinations; at the same time the purity of the gas could be tested.

### § 2. *The measuring apparatus.* (See Pl. I).

In the vapour pressure apparatus of the small pattern *A* about 120 cc. gas can be condensed, in the large pattern *B* about 1 Liter. Pattern *A* consists of a bulb *a* of 0.5 cc. with a glass stem *b*, connected to a manometer with a steel capillary *c*. The manometer consists of two tubes $m_1 m_2$ of 2 cm. bore filled with mercury; they are connected by an india rubber tube. An air-trap *d* prevents impurities from coming into the gas. The glass stem is moreover surrounded by a copper cylinder *e* and a glass jacket *f* by means of which heat is conducted from above, thus preventing the temperature at any part of the apparatus from falling below that of the bulb which is placed in the cryostat at the place where the temperature is measured. By pressing the mercury higher up or lower down one can condense different quantities of gas successively.

The construction of pattern *B* differs a little from that of *A*; this is especially in order to avoid the apparatus becoming difficult to handle because a too large quantity of mercury would be required. The manometer $m_1m_2$ consists of a *U*-tube of glass of which the two limbs are separated by a glass cock $k_1$. This *U*-tube is blown on to another $d_1d_2$ which contains the gas. The two limbs of the latter are cylinders of 70 c.m. length and 0.5 liter contents separated by a cock $k_2$. The limb $d_1$ connected to the manometer is fixed at its upper end to the steel capillary *c* which is connected with the bulb *a*. The limb $d_2$ carries a glass cock $k_2$, through which the apparatus is filled. The reservoir is filled to 1 atm. excess of pressure with gas. By first shutting $k_2$ and then opening it we can condense first the gas of $d_1$ which is under an excess of pressure, then also that of $d_2$.

*A* enables us to judge of the purity of the gas when we investigate in how far the vapour pressure measured depends on the fraction of the quantity of gas already condensed. By means of *B*, where the quantity of condensed gas always amounts to the same portion of the total quantity, we can determine in how far the vapour pressure is independent of the increase or decrease of the quantity of the condensed gas itself.

The oxygen is prepared by heating potassium permanganate. After it has been carefully purified and dried over a KOH-solution and $P_2O_5$ the gas is condensed in a bulb immersed in liquid air. Then the liquid air is removed and the apparatus are filled with the evaporated gas.

The pressure was read with a cathetometer; this does not require a very high degree of accuracy because of the great variability of the vapour pressure with the temperature. The atmospheric pressure on the mercury in the open manometer was read on an aneroid barometer which we occasionally compared with a mercury barometer.

§ 3. *The determination of temperature and the degree of accuracy.* For measuring the temperature we have used for the determinations in the neighbourhood of the boiling point of oxygen the resistance thermometer $Pt'_I$ which has been compared [1]) (comp. Comms. N°. 95*c* and N°. 101*a*) over a large range with the hydrogen thermometer of Comm. N°. 95*e* which we shall call $B_{III}$; for — 182° this was done on March 25th 1907 (comp. Comm. N°. 101*a* table I) Some calibrations have afterwards been made, which together with those just named are given in table II. This table also contains the results of indirect comparison of $Pt'_I$ with another hydrogen thermometer, which we call $T_4$ and which was used in an investigation of Dr. FEUSTEL and one of us (K. O.) with a differential thermometer helium-hydrogen, which investigation is in calculation and as we hope can soon be published.

In connection with § 4 of Comm. N°. 101*a* we have also given in table I the results of 4 comparisons between two resistance thermometers $Pt'_I$ and $Pt''_d$ [2]) at about — 183° C. and — 217° C.

TABLE I. Comparison between $Pt'_I$ and $Pt''_d$.

| Date | $Pt'_I$ | $Pt''_d$ | $Pt'_I$ and $Pt''_d$ in degrees |
|---|---|---|---|
| 22 June '07 | 34.267 | 18.565 [3]) | 0°.000 |
| 18 Dec. '07 | 34.359 | 18.609 | |
| 24 June '07 | 14.761 | 9.1483 [3]) | 0°.007 |
| 19 Dec. '07 | 14.824 | 9.1793 | |

For the measurements on 18th and 19th Dec. '07 $B_{III}$, $Pt'_I$ and

---

[1]) $W_{PtI} = 1.01806\ W_{Pt'I}$ (comp. § 2 of Comm. N°. 101*a*).

[2]) This resistance thermometer is the same as the one which in Comm. N°. 99*b* is called $Pt_d$. Afterwards it has broken in the middle, and consequently the resistance was diminished to half its value ($Pt'_d$) Here it is indicated with two accents because it has then undergone a small reparation owing to which $Pt''_d = 1.00073$ $Pt'_d$ at 0°.

[3]) This value has been reduced with the factor of the preceding footnote.

$Pt''d$ were placed in the cryostat. Thus we simultaneously obtained the results relating to them of the tables I en II. Those of the second part of table II are derived from a comparison between $Pt''d$ and $T_4$. The resistances observed were reduced with the factor 1.00073 (cf. the footnote on the preceding page), giving 18.560 and 18.398 Ω. These have been reduced with the data of table I to $Pt'_I$. This yields the values of the third column.

The calibration of $T_4$ agrees satisfactorily with that of $B_{III}$. The mean of the deviations for the two former and the two latter data differs from table II by 0.022 Ω, which corresponds to 0°.038. This small difference between the readings of two entirely different gas

TABLE II. Comparison of the resistance thermometer $Pt'_I$ with the hydrogen thermometers $B_{III}$ and $T_4$.

| Date | Temperature according to the hydrogen thermom. $B_{III}$ | Resistance in Ω | $O_{Pt'_I} - C_{A_I}$ |
|---|---|---|---|
| | Comparison with $B_{III}$. | | |
| 25 March '07 | — 182°.352 | 34.492 | — 0.008 |
| 18 Dec. '07 | — 182°.595 | 34.359 | — 0.000 |
| 17 Febr. '08 | — 186°.599 | 32.027 | — 0.019 |
| 18 Febr. '08 | — 189°.500 | 30.332 | — 0.041 |
| 19 Dec. '07 | — 216°.840 | 14.824 | + 0.031 |
| | Comparison with $T_4$. | | |
| 30 Nov. '07 | — 182°.736 1) | 34.257 | — 0.021 |
| 3 Dec. '07 | — 183°.302 1) | 33.919 | — 0.031 |

---

1) The hydrogen thermometer temperatures are calculated on the scale of Comm. N°. 95*e*. As the zero pressure amounted to about 1360 mm. we have accordingly accepted for the coefficient of pressure variation 0.0036629, derived from the coefficient of pressure variation of Comm. N°. 60 (0.0036627 for 1100 mm. zero pressure). We have also applied a correction according to the difference of the correction to the absolute scale for 1360 and 1100 mm. zero pressure.

thermometers satisfactorily confirms our statement (Comm. N⁰. 95*e*) concerning the limit of accuracy and enhances the reliability of the preceding determinations of temperature.

The tables I and II also give new data about the accuracy of the readings of the resistance and of the gas thermometer [1]). According to table I the error of the resistance remains below 0.°01. As to the readings of the gas thermometer, the first two data of table II inter se yield a difference smaller than 0.°02. With the difference + 0.031 Ω at — 217° correspond + 0.028 and + 0.016 of table II in Comm. N°. 95*c* and table I in Comm. N⁰. 101*a*. This also agrees with the limit of accuracy 0.°02 derived in § 7 of Comm. N⁰. 95*e*. This seems not to be the case for the value of 18 Febr. '08 which deviates rather much from the formula. It will depend on later determinations what part of this deviation must be ascribed to the formula $A_I$.

§ 4. *The vapour pressure determinations in the neighbourhood of the boiling point of oxygen.*

We have used the cryostat described in Comm. N⁰. 94*f* (Pl. V) The temperature was determined and regulated with the resistance $Pt'_I$ placed in the bath. The deviations of the galvanometer were so small that no correction was required for it. In the apparatus *A* the mercury was raised successively in the lower and the upper end of the manometer $m_1$, in *B* first the gas of one reservoir was condensed, afterwards of the two reservoirs. This is indicated in the following table with "little" and "much". Table III contains a determination at a small excess of pressure, another at a pressure of a little below 760 m.m. and a determination for control also at an excess of pressure. The pressure is reduced to 0° C. as regards the temperature of the mercury. The last column contains the deviations from the mean for each series.

The resistance of the thermometer read on the Wheatstone bridge were for the three series respectively:

34.433 , 34.098 and 34.433 Ω.

If we compare the results obtained with the condensation of a little quantity of gas with those with the condensation of a large quantity we cannot find any systematical deviations, which speaks for the purity of the gas used. In case impurities should occur their influence on the vapour pressure derived with the smaller condensation is sure to be less than the influence on the difference just mentioned. It may therefore be neglected.

---

[1]) Comp. Comms. No. 95*c*, 95*e* and 101*a*.

TABLE III. Vapour pressure of oxygen in the neighbourhood of the boiling point.

| Date | Time | | Pressure in m.m. mercury | Mean of a series | Deviation from the mean |
|---|---|---|---|---|---|
| 6 Febr. '08 | $4^h\ 31'$ | large pattern (little) | 806.34 | 806.71 | −0.37 |
| excess of pressure | 4 46 | small „ (much) | 806.55 | | −0.16 |
| Series I | 5 0 | „ „ (little) | 806.98 | | +0.27 |
| | 5 8 | large „ (much) | 806.97 | | +0.26 |
| 7 Febr. '08 | 10 13 | small „ (little) | 759.47 | 759.61 | −0.14 |
| pressure a little below 760 mm. | 10 21 | „ „ „ | 759.75 | | +0.14 |
| Series II. | 10 50 | „ „ (much) | 759.46 | | −0.15 |
| | | | 759.54 | | −0.07 |
| | 11 12 | large „ „ | 759.35 | | −0.26 |
| | | | 759.51 | | −0.10 |
| | 11 47 | „ „ „ | 759.76 | | +0.15 |
| | 12 26 | small „ (little) | 759.84 | | +0.23 |
| | 12 37 | large „ (much) | 759.82 | | +0.21 |
| 7 Febr. '08 | 1 20 | small „ (little) | 806.17 | 806.26 | −0.09 |
| excess of pressure | 1 25 | large „ (much) | 806.30 | | +0.04 |
| Series III. | 1 35 | small „ (little) | 806.31 | | +0.05 |

## § 5. *Accuracy of the adjustments.*

From the results of table III we derive the following data.

The deviations from the mean which must be ascribed partly to the regulation of the temperature are small and when reduced to differences of temperature they remain below 0°.005.

The mean of the results of the large and the small pattern derived separately for each series gives:

Series I, large pattern $p = 806.65$ (2 observations)
small „ 806.76 (2 „ )
Series II, large „ $p = 759.64$ (5 „ )
small „ 759.58 (4 „ )
Series III, large „ $p = 806.30$ (1 observation)
small „ 806.24 (2 observations)

The difference between the two means is at the utmost 0.1 mm, which corresponds to $\frac{1^\circ}{800}$. Thence we may conclude that a vapour pressure apparatus is extremely suited for the standardizing of temperatures. The data obtained here show that in this respect the apparatus surpasses the gas thermometer and probably also the resistance thermometer. For the hydrogen thermometer, namely, the error of 2 adjustments amounts to 0°.01 à 0°.02 (comp. § 3 and Comm. N⁰. 95*e* § 8 and N⁰. 101*a* § 3), for the resistance thermometer to 0°01 (comp. § 3 and Comm. N⁰. 101*a* § 4) [1]).

## § 6. *The determination of the boiling point of oxygen.*

With the resistances of $Pt'_I$ given in § 4 we can by means of the data of table II derive the corresponding temperatures on the scale of our hydrogen thermometer $B_{III}$. To this end we start from the mean of the two data of March 25 and Dec. 18, '07, because these are probably more accurate than those obtained with the thermometer $T_4$. To 34.433 and 34.098 Ω correspond the temperatures — 182°.460 and — 183°.040 respectively. To the first belongs the vapour pressure 806.40 m.m. (the mean from the series I and III), to the second 759.61 mm. (series II). Thence follows by means of rectilinear interpolation for 760 mm. at Leiden for the temperature on the thermometer $B_{III}$ : $t = -183°.035$ and for the normal boiling point (760 mm. on sea-level and 45° northern latitude):

---

[1]) The data of table III also enable us to judge of the accuracy of the adjustment of the resistance. Let the error in the reading of vapour pressure apparatus = 0, which approximately is permissible according to what precedes, then the difference of the means for the series I and III must be ascribed to the error of the measurement of the resistance. This then would be 0°.005.

$$t = -183°.030 - 0°.007 = -183°.037$$

on the normal hydrogen thermometer and (comp. table XXV of Comm. N⁰. 101*b*)

$$\theta = -183°.042 + 0°.056 = -182°.986$$

on the absolute scale.

If we take into consideration the degree of accuracy of the correction to the absolute scale (comp. Comm. N⁰. 97*b*) and the results for the control determinations for the measurement of temperature made as well with the same hydrogen thermometer as with different ones, then it follows that this value does not probably deviate from the real value by more than 0°.03.

§ 7. *Vapour pressure determination at lower temperatures.*

For these measurements (comp. § 2 and table II) the temperature was directly read on the hydrogen thermometer $B_{III}$; $Pt'_I$ was used for the regulation. The temperatures are — 186°.599 and — 189°.500 (comp. table II). At the same time we obtained a new calibration for $Pt'_I$. The determinations were made with only the small vapour

TABLE IV. Vapour pressure of oxygen below the boiling point.

| Date | Time | Pressure in mm. | Mean of a series | Deviation from the mean |
|---|---|---|---|---|
| | h | | | |
| 17 Febr. '08 *(a)* | 2 55′ | 366.06 | 365.99 | +0.07 |
| *(a)* | 3 30 | 365.90 | | —0.09 |
| *(b)* | 4 5 | 366.00 | | +0.01 |
| *(b)* | 4 25 | 365.98 | | —0.01 |
| 18 Febr. '08 *(a)* | 10 42 | 515.82 | 515.83 | —0.01 |
| *(a)* | 11 6 | 515.89 | | +0.06 |
| *(b)* | 11 30 | 515.69 | | —0.14 |
| *(b)* | 11 40 | 515.94 | | +0.11 |

pressure apparatus. The results are combined in table IV in the same way as in table III.

In the determinations marked ($a$) about half of the gas was condensed, in those marked ($b$) about $\frac{4}{5}$ of the gas. As was the case for the boiling point no systematic difference resulting from this seems to be perceptible. If we reduce the temperatures to the absolute scale and the pressures to sea-level and 45° northern latitude we find for:

$$\theta = -186°.542 \qquad p = -516.19 \text{ mm.}$$
$$\theta = -189°.442 \qquad p = -366.24 \text{ mm.}$$

§ 8. *The results compared with those of other observers.*

Of previous determinations those by Travers, Senter and Jaquerod[1]) deserve most confidence, especially because these observers used pure oxygen in a closed reservoir. This is not the case with the other observations where the temperature of a bath of oxygen boiling under atmospheric pressure was determined. For then impurities, nitrogen as well as less volatile substances are unavoidable. It seems that the influence of the latter is paramount; all these results for the boiling point are too high by 0°.3 or more. The first mentioned determinations yield for the boiling point of oxygen — 182°.93 on the normal hydrogen scale. For the pressure 760 mm. is given without indication of a further reduction. Our value for 760 mm. mercury (at 0°) is on the normal hydrogen scale —183°.030, differing by 0°.10 from the value mentioned above. One of the last determinations is that of Grunmach [2]). He finds — 182°.23. With the correction derived by Hoffmann and Rothe [3]) for the pentane thermometer (— 0°.42) this becomes — 182°.66, a result which after being corrected is still much too high.

If we compare the two observations at lower pressure with those of Travers, Senter and Jaquerod then it appears that both our temperatures are lower by 0°.13. Hence it is clear that a systematic difference exists between the two series.

---

[1]) Phil. Trans. A 200, 1902.

[2]) Berliner Sitz. Ber. 1906.

[3]) Zeitschr. f. Instrkd. 27, 1907.

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PROF. DR. H. KAMERLINGH ONNES,
*Director of the Laboratory.*

## No. 107$^b$.

**Dr. H. KAMERLINGH ONNES and J. CLAY.** "On the measurement of very low temperatures. XXII. The thermoelement gold-silver at liquid hydrogen temperatures"

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam*, **30 Mei 1908**, pp. 94—95.)

EDUARD IJDO — PRINTER — LEIDEN.

### **Dr. H. KAMERLINGH ONNES and J. CLAY.** — "*On the measurement of very low temperatures.* XXII. *The thermoelement gold-silver at liquid hydrogen temperatures*".

The thermoelement gold-silver of which the thermoelectric power at ordinary temperature is about zero, shows at lower temperatures a rapidly increasing sensitivity [1]).

A calibration with the hydrogen thermometer has shown that at the temperatures which can be reached with liquid and solid hydrogen the increase of the electromotive force of this thermoelement per degree becomes large enough to render it suitable for temperature determinations in the area under consideration, while at the temperatures far below the melting point of hydrogen (for the determination of which the helium thermometer must be used for the calibration instead of the hydrogen thermometer), the sensitivity of the instrument will be greater still.

The following table may serve to make this clear.

TABLE I. Calibration of the thermoelement gold-silver at liquid hydrogen temperatures.

| Temperature read on the hydrogen thermom. | Electromotive force in millivolts. | |
|---|---|---|
| | gold-silver | (constantin-steel) |
| (—216°.01) | (0.11972) | |
| (—217.42) | | (6.8310) |
| —252.86 | 0.24742 | |
| —252.93 | | (7.1315) |
| —255.34 | 0.26304 | |
| —258.61 | 0.28912 | |
| —259.24 | | (7.1585) |

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[1]) Comp. the measurements of J. Clay in his thesis for the doctorate and in Comm. N°. 107*d*.

The third column contains the determinations of the electromotive force of the element constantin-steel of Table VI in Comm. N⁰. 95*a*. Owing to the great lessening of the increase of the electromotive force per degree this element is unfit for the accurate measurement of the lowest temperatures [1]).

We shall soon publish a calibration of the thermoelement gold-silver with the helium thermometer at low temperatures.

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[1]) Also the element germansilver-platinum investigated by DEWAR (Proc. Roy. Soc. A 76 p 316 sqq. 1905) is unfit for this purpose on account of the same defect.

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PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

## No. 107c.

**Dr. H. KAMERLINGH ONNES and J. CLAY.** "On the change of the resistance of pure metals at very low temperatures and the influence exerted on it by small amounts of admixtures. II".

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam*, **30 Mei 1908**, p. 95—96).

EDUARD IJDO — PRINTER — LEIDEN.

## **Dr. H. KAMERLINGH ONNES** and **J. CLAY**. "*On the change of the resistance of pure metals at very low temperatures and the influence exerted on it by small amounts of admixtures.* II" 1).

§ 7. *Supplementary notes to Comm. No. 99c.*

*Gold.* For the gold that by the analysis has been proved to be the purest (the impurity amounted only to circa 0.005 %) and of which the resistance has been given in table I, 2nd col., two formulae have been calculated, of the following form 2):

$$\frac{W_t}{W_0} = 1 + a\left(\frac{t}{100}\right) + b\left(\frac{t}{100}\right)^2 + c\left(\frac{t}{100}\right)^3 + e\left(\frac{10^6}{T^3} - \frac{10^6}{(273.09)^3}\right) + \\ + f\left\{\frac{10^{10}}{T^5} - \frac{10^{10}}{(273.09)^5}\right\}.$$

The deviations between the observed values and those given by the formula, can be found in the 3d and 4th col. of table I.

---

1) In this translation have been inserted the observations, formulae and further particulars given by J. CLAY in his thesis for the doctorate, Leiden 1908.

2) It has already been pointed out (Comm. Nos. 93, 95 etc.) that the resistance below 0° C. cannot be represented by a parabolic formula, as was also noted by other observers. It appears that it is impossible by means of any polynomials with positive powers of $t$ to obtain a formula also applicable to liquid hydrogen temperatures and it is necessary to insert negative powers of $T$.

Calculation had shown (Comm. N⁰. 99*c*) that in some cases, e.g. silver and gold, terms with higher reciprocal powers of $T$, such as the 3d and 5th, were more satisfactory than the 1st and 2nd. At all events it appears most clearly from all observations, that to include in one formula the resistance over the whole region of low temperatures we must resort to rather intricate formulae.

The reciprocal powers of $T$ amount to the same, in fact, as the exponential factor proposed by KOENIGSBERGER (Jahrbuch der Radioactivität und Electronik 4, p. 158) for metallic oxides and sulphides, which should also be valid for metals. If we consider the therms with the reciprocal powers of $T$ as the first terms of the exponential series, we should be able, according to KOENIGSBERGER'S view, to determine from the coefficients of these terms, the degree of dissociation of the electrons from the atoms of the metal.

TABLE I. Pure gold.

| Temperature | Observed resistance. | O—C (orig. 1st sol.) | O—C (orig. 2nd sol.) | O—C (1st gener. sol.) |
|---|---|---|---|---|
| 0° | 1 | 0 | 0 | 0 |
| — 102.99 | 0.59306 | 0 | $-\,0.0_{2}004$ | — 0.01246 |
| — 183.00 | 0.27096 | 0 | $+\,0.0_{2}402$ | — 0.01990 |
| — 197.87 | 0.20871 | $+\,0.0_{2}054$ | $+\,0.0_{2}139$ | — 0.02213 |
| — 205.01 | 0.17897 | $+\,0.0_{2}129$ | $+\,0.0_{2}002$ | — 0 02290 |
| — 215.34 | 0.13337 | 0 | +0.01433 | — 0.02652 |
| — 252.93 | $0.0_{2}8103$ | $+\,0.0_{2}002$ | 0 | — 0.01986 |
| — 255.13 | $0.0_{2}5691$ | $-\,0.0_{2}259$ | $+\,0.0_{2}110$ | — 0.01938 |
| — 258.81 | $0\ 0_{2}3601$ |  | 0 | — 0.01402 |
| [— 261] | $0.0_{2}2713$ |  | $-\,0.0_{2}175$ |  |
| [— 262] | $0.0_{2}2526$ |  | 0 |  |

Table I, 5th col. and table II, last line, will be referred to in Comm. No. 107*d* § 6.

The values of the coefficients are given in table II.

TABLE II.

| Pure Gold | *a* | *b* | *c* | *e* | *f* |
|---|---|---|---|---|---|
| 1st sol. | + 0.409047 | + 0.023553 | + 0.0098130 | $+\,0.0_{3}604180$ | $-\,0.0_{5}791022$ |
| 2nd sol. | + 0.375282 | — 0.026147 | — 0.0067008 | $+\,0.0_{3}153462$ | $-\,0.0_{5}114129$ |
| 1st general sol. | + 0.383596 | $+\,0.0_{2}40678$ | $+\,0.0_{2}345802$ | $+\,0.0_{3}323307$ | $-\,0.0_{5}40547$ |

To investigate especially the influence of the diameter of the wires, we have measured also the resistance of a piece of wire of a diameter of 0.5 m.m., drawn from the same gold of which the resistance has been given in Comm. N$^{0}$. 99*c*, table I, 3d col.

We found

| Temperature. | Resistance wire 0.1 m.m. | Resistance wire 0.5 m.m. |
|---|---|---|
| 0° | 1 | 1 |
| — 103.83 | 0.59389 | 0.59179 |
| — 255.13 | 0.006459 | 0.005909 |

As for the difference in hardness that these wires may show, this cannot after MATTHIESSEN's opinion (Pogg. Ann. 122, page 68) influence the coefficient of temperature, though the absolute value of the resistance may be slightly varied by it. A small difference in purity is here, too, probably the cause of the difference in resistance. Finally, similar measurements were made for two wires of different diameter of the same gold, and moreover, after the measurements, we had the relative purity of the wires determined by analysis as a control.

The impurity of the thin wire was found by Dr. v. HETEREN to be 0.072 % larger than that of the thick one.

The diameter of wire A was 0.1 m.m., of B 0.3 m.m. The results of the resistance-measurements are the following:

TABLE III.

| Temperature. | A | B | Difference |
|---|---|---|---|
| 0° | 1 | 1 | |
| — 103.63 | 0.59595 | 0.59667 | — 0.00072 |
| — 183.65 | 0.28612 | 0.28169 | 0.00443 |
| — 216.61 | 0.14902 | 0.13871 | 0.01031 |
| — 252.78 | 0.02988 | 0.01856 | 0.01132 |
| — 258.70 | 0.02443 | 0.01511 | 0.01132 |

at 0° the resistance of A is $W_0 = 8.3030$
of B is $W_0 = 3.4103$.

*Mercury.* The values, given in Comm. No. 99*c* (except that for 0°) are represented by the quadratic formula:

$$W_t = 22.3605\ (1 + 0.003581\ t - 0.0_6 588\ t^2)$$

which for — 197.°87 gives O — C = + 0.0106, so that we are led to think, that the temperature has not been observed quite accurately enough. Of the metals investigated mercury seems to be most fit for the measurement of temperatures below the melting point of hydrogen.

The difference between formula and observation is given in table IV.

TABLE IV. Change of the resistance of pure mercury, in solid state, with the temperature.

| Temperature. | Resistance. | O—C |
|---|---|---|
| 0° | 97.162 | |
| — 183.00 | 7.2650 | 0 |
| — 197.87 | 6.0103 | + 0.0106 |
| — 205.01 | 5.3900 | 0 |
| — 215.34 | 4.5057 | 0 |
| — 252.93 | 1.2613 | 0.0025 |
| — 258.81 | 0.7534 | 0 |

Comparing our results at low temperatures with those of Dewar and Fleming (Proc. Roy. Soc. 60 1896 p. 76) according to their observations we should have found at — 197.°9 7.19 Ω
and at — 183.°00 8.35 Ω.

Thence follows, that probably their mercury was not as pure as ours. It is true that their temperatures have been derived from the platinumscale, but the differences in temperature, that issue from this, are small in any case in comparison to the observed differences in resistance.

*Lead.* Two formulae, of the form $A'$ and $B'$ $\{A$ and $B$ with omission of the therm $c\left(\frac{t}{100}\right)^3\}$ have been calculated for lead, according to which we must reject the observation at — 255° 07, being 0.02314, where $A'$ gives 0.01974 and $B'$ 0.01984

TABLE V. Change of the resistance of lead with the temperature.

| Temperature. | Resistance. | $O-C_{A'}$ | $O-C_{B'}$ |
|---|---|---|---|
| + 16°.33 | 1.0652 | | |
| 0° | 1 | 0 | 0 |
| — 103.63 | 0.59548 | 0 | 0 |
| — 183.65 | 0.29439 | — 0.00059 | — 0.00043 |
| — 195.15 | 0.25252 | + 0.00028 | + 0.00035 |
| — 204.52 | 0.21742 | 0 | 0 |
| — 216.61 | 0.17129 | — 0.00105 | — 0.00114 |
| — 252.78 | 0.03032 | 0 | 0 |
| — 255.07 | 0.02314 | | |
| — 258.70 | 0.01311 | — 0.00144 | 0 |

§ 8. *Carbon and constantin.* In conclusion we have to mention the results of the investigation on the change of the resistance of two materials, which, for the rest, are not related to the preceding, viz. of carbon and constantin.

The constantin was wound, in the form of a wire, round a glass cylinder whereas for the carbon a filament of an electric lamp was used. The results are given in table VI.

## TABLE VI.

| Temperature. | Resistance constantin. | Resistance carbon. |
|---|---|---|
| + 100° | | 0.89899 |
| + 13.30 | 1.00849 | |
| 0 | 1.— | 1.— |
| — 102 99 | | 1.15888 |
| — 182.42 | 0.97165 | |
| — 252.93 | | 1.22522 |
| — 255.13 | 0.91423 | 1.23951 |
| [— 262] | 0.89978 | |

The resistance of constantin at 0° was 66.015 Ω, and of the carbon filament 77.524 Ω.

## TABLE VII.

| Temperature. | *Pt* | *Au*$_V$ | *Au*$_0$ | *Ag* | *Pb* | *Bi* | *Hg* |
|---|---|---|---|---|---|---|---|
| 0° | 0 | 0 | 0 | 0 | 0 | 0 | |
| — 30.53 | — 0.00975 | | | | | | |
| — 58.58 | — 0.01864 | | | | | | |
| — 87.55 | — 0.02950 | | | | | | |
| — 103.63 | | | | | — 0.02505 | + 0.01625 | |
| — 103.83 | — 0.03635 | — 0.02674 | — 0 01465 | — 0.03900 | | | |
| — 139.87 | | | | — 0.05500 | | + 0.04086 | |
| — 140.19 | — 0.05345 | | | | | | |
| — 159.11 | — 0.06369 | | | | | | |
| — 182.79 | — 0.07783 | | | | | + 0.08369 | |
| — 183.00 | | — 0.05893 | | | | | — 0.004987 |
| — 183.60 | | | | — 0.08101 | — 0.03312 | | |
| — 195.15 | — 0.08531 | | | — 0.08830 | — 0.03283 | + 0.09945 | |
| — 197.87 | | — 0.06673 | — 0.03636 | | — 0.03367 | | — 0.006500 |
| — 204.67 | — 0 09076 | | | — 0.09526 | | + 0.11014 | |
| — 205.01 | | — 0.07033 | — 0.03938 | | | | — 0.008245 |
| — 212.63 | — 0.09651 | | | | | | |
| — 215.34 | | — 0.07810 | — 0.04466 | | | | — 0.009907 |
| — 216.65 | — 0 09651 | | | | — 0.03553 | + 0.12112 | |
| — 252.78 | — 0.06001 | | | | — 0.04405 | | |
| — 252.92 | | — 0.065717 | — 0.02828 | — 0.064947 | | + 0.14976 | — 0.017337 |
| — 255.18 | — 0.05341 | — 0.060079 | | | — 0.04280 | + 0.14888 | |
| — 258.81 | | — 0.048689 | — 0.01247 | | — 0.03958 | + 0.14363 | — 0.018597 |
| — 259.10 | — 0.04070 | | | — 0.043848 | | | |

It has been proved, that the decrease of the resistance of constantin accelerates at lower temperatures. For carbon too the change below 0° proves to be much larger than above 0°.

*Survey.* To give a survey of the change of the resistance of pure metals with the temperature, table VII has been inserted. For that purpose the difference has been calculated between the observed resistance and the resistance which we calculate, starting from that at 0° C, and supposing that the change is proportional to the absolute temperature. To Comm. N⁰. 107*d* a diagram has been adjoined, in which also the values of table VII are inserted.

In this diagram the pure metals, as mentioned in Comm. N⁰. 107*c*, except bismuth, show a positive deviation, and all the alloys of gold and silver show a negative deviation. The type however of the curves for the pure metals (except bismuth) and for the alloys is the same. The curves are all bending upward from 0° C. till about — 200° C., and bending downward in the region of the liquid hydrogen temperatures.

The curves for the pure metals, also for the purest gold, will, when prolonged, intersect the temperature-axis before the absolute zeropoint, and seem to indicate all a large negative value at this point.

The curve for mercury only, which is (in comparison to other metals) so little beneath its meltingpoint, and besides probably the purest of the investigated metals on account of being repeatedly distilled in vacuo, does not bend downward as yet. The deviations have been calculated regarding to a resistance at 0°, that was extrapolated from the values of the resistance at low temperatures.

Moreover the straight shape of the curve is remarkable. Accordingly, if we can overcome the practical difficulties, mercury would be (as also the calculation with the quadratic formula in § 7 has proved already) extremely well fit as a thermometric metal, especially also because a greater purity can be obtained than for other metals.

For all metals, except mercury, a point of inflexion has been found, of which the temperature has been determined more accurately by means of a formula. Further, for none of the metals, nor for the alloys, has the minimum been experimentally determined up to now, although one is shown in the diagram constructed by KOENIGSBERGER (Jahrb. der Radioaktivität und Electronik IV, Heft 2, p. 179) according to the values observed by us.

It is true that the curve, representing the observed resistances as a function of the temperature, and being computed so as to give an infinitely large value for the resistance at — 273°, will show a minimum; this minimum, however as regards temperature always lies beneath the limit of observation as yet.

This may excite a doubt of Lord KELVIN's opinion, that the resistance at the absolute zeropoint does not become zero, but may have a very large value, but this opinion has been supported in these days by the conduct of sulfides and oxides of metals, zirconium and silicium (cf. KOENIGSBERGER, Jahrbuch der Radioaktivität und Electronik IV, p. 158).

§ 9. *Alloys of Au and Ag.* One of us (J. CLAY) has extended the investigation treated of in the preceding sections to different alloys of gold and silver and has added the determination of the electromotive force of the thermoelement gold-silver. This investigation showed that the theories of RAYLEIGH and LIEBENOW about the thermoelectric origin of the difference in resistance introduced in § 1 (the additive resistance of MATTHIESSEN ¹)), must be rejected. For the value $p$, introduced in § 1, the observations mentioned yield with a gold wire of 1 m. in length and 1 mm.$^2$ in section per volume procent silver added

$$p = 0.00360\ \Omega.$$

§ 10. *Amalgams* [added in this translation]. In the investigation the influence of small admixtures we have been much hampered by the incertainty about the chemical nature of the admixture, the process of drawing the metal into wires introducing new contaminations. The same incertainty was found in the investigation of the alloys (Comm. N$^0$. 107*d*). Therefore we have taken in hand the investigation of the influence of small quantities of

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¹) With regard to the deviation from MATTHIESSEN's theorem at liquid hydrogen temperatures, mentioned sub § 1, we also refer to the publications mentioned in the footnote 2 of p. 20 Comm. No. 99*c*).

another metal dissolved in mercury, where all difficulties of drawing and contact with other metals, are eliminated. Some indications point to the fact that the nature of the impurity does not much matter in the value of $p$. This may be discriminated in the best way by experiments with mercury containing small admixtures of different kind.

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

OF THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,
*Director of the Laboratory.*

## No. 107$^{d}$.

**Dr. J. CLAY.** "On the change with temperature of the electrical resistance of alloys at very low temperatures". (*With a plate.*)

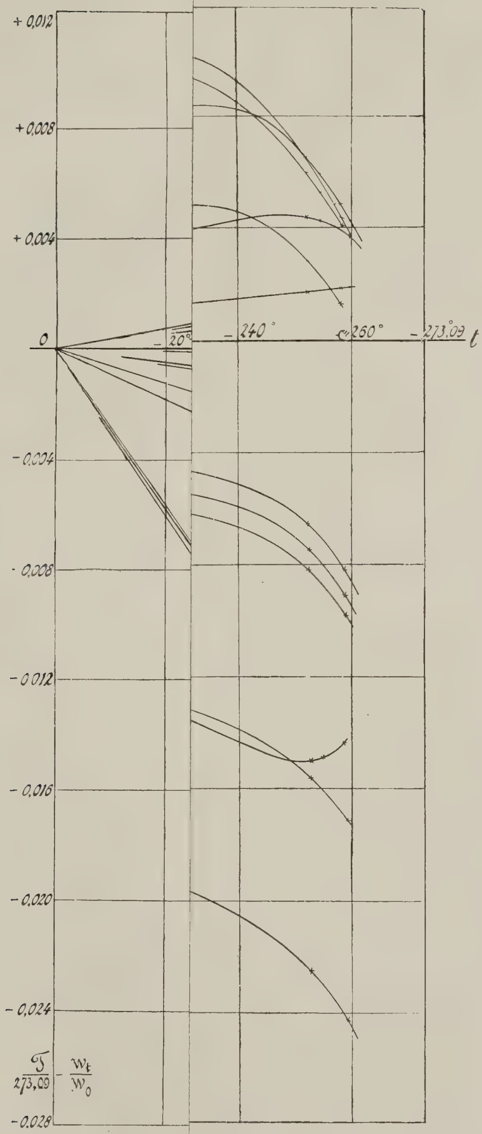
(*Translated from the Thesis for the doctorate*, **5 Juni 1908**).

EDUARD IJDO — PRINTER — LEIDEN.

**Dr. J. CLAY.**

**low tempera**

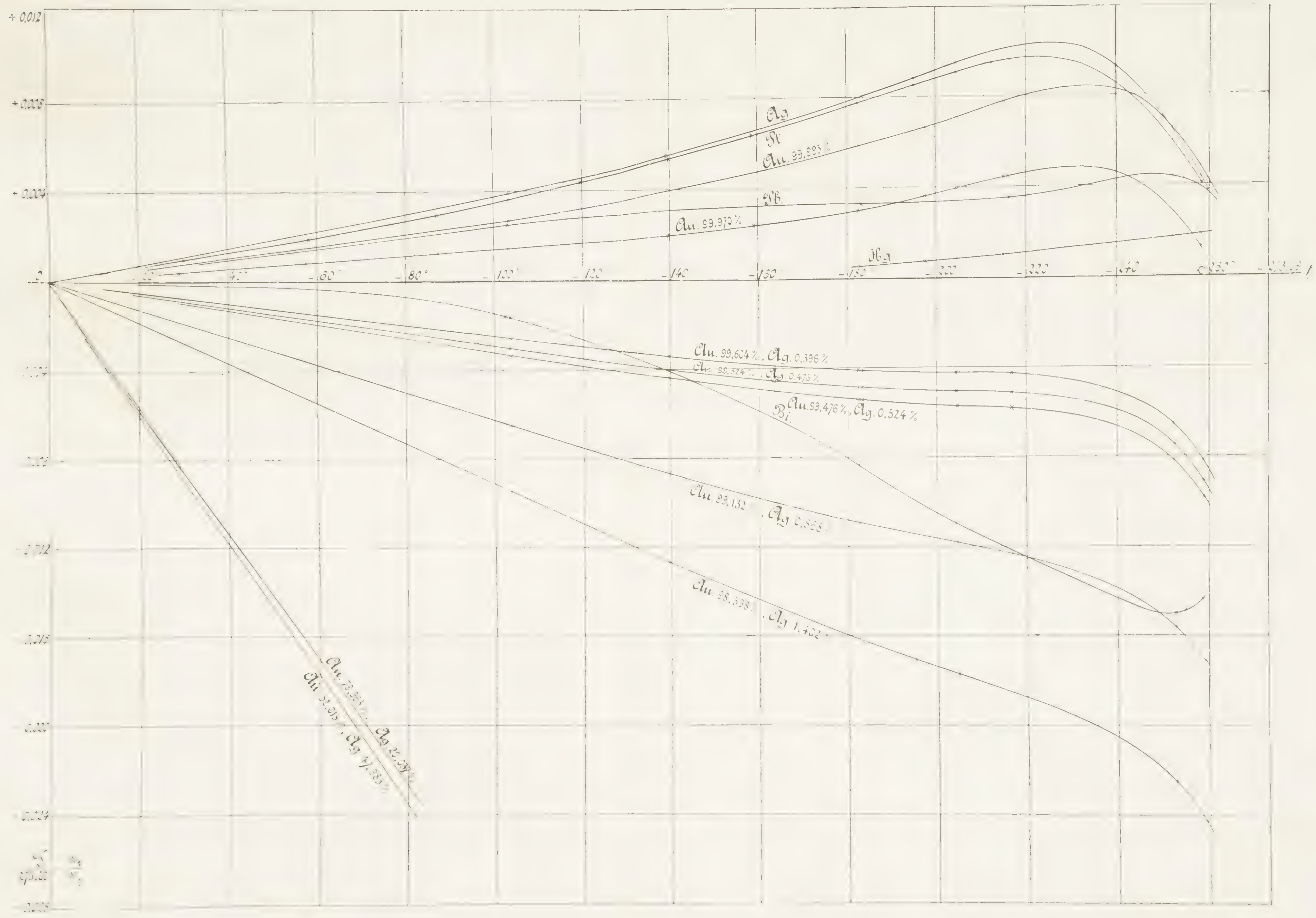
## PLATE I.



Communicat

**Dr. J. CLAY.** "On the change with temperature of the electrical resistance of alloys at very low temperatures".

PLATE I.



Communication No. 107$^{d}$

## **Dr. J. CLAY.** "*On the change with temperature of the electrical resistance of alloys at very low temperatures.*"

§ 1. *Introduction.* The present Comm. as announced in Comm. No. 107*c* § 9 extends the investigation of the influence of small admixtures on the change with temperature of the electrical resistance of pure metals. A first alloy, in which there was good reason to consider that the admixture to the gold was silver, had been investigated by KAMERLINGH ONNES and myself in Comm. No. 99*c*. I have now systematically investigated this influence of admixtures in the case of a number of definite alloys of gold with a small quantity of silver. The first metal was chosen (Comm. No. 99*c* § 1), because as minting material it is prepared extremely pure, it is not easily attacked chemically and is easily drawn into wires. Silver has to a certain extent the same advantages. Besides, accurate measurements of the resistance of gold and silver as well as of their temperature coefficient between 0° and 100° C. already exist.

§ 2. *Investigations by others.*

The electrical resistances of a great number of alloys of various compositions, amongst them alloys of gold and silver, were investigated by MATTHIESSEN [1]) and by MATTHIESSEN and VOGT [2]).

MATTHIESSEN divides metals into two classes, viz.: *a.* those metals which when alloyed with one of the same class have a resistance compounded from the resistances of the components in the ratio of their relative volumes, and *b.* those metals which when alloyed with one of the class *a* or with one of the same class, have a resistance much larger than that determined by the simple law of mixtures.

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1) A. MATTHIESSEN. Pogg. Ann. 110 (1860) p. 190.

2) A. MATTHIESSEN and C. VOGT. Pogg. Ann. 122 (1864) p. 19.

Not only is the resistance at a definite temperature very much modified by a small amount of a metal of class *b*, but also the temperature coefficient of the resistance changes [1]).

Matthiessen and Vogt made a systematical investigation of the temperature coefficients of the resistances of the same alloys between 0° and 100° C. From their determinations they derive an empirical relation between the resistances observed at different temperatures, and those calculated for the same temperatures from the relative volumes of the components, e. g.

$$W_{100^\circ} - W_{0^\circ} = W'_{100^\circ} - W'_{0^\circ}$$

and, more generally, as 100° and 0° are only arbitrary temperatures:

$$W_t - W'_t = \text{const}$$

$W_{100^\circ}$, $W_{0^\circ}$, and $W_t$ are the observed resistances, $W'_{100^\circ}$, $W'_{0^\circ}$, $W'_t$ are the resistances calculated from the relative volumes of the components according to the simple law of mixtures.

Fleming [2]) in a research extending to a temperature of — 190° C. observed that the curve representing resistance as a function of temperature seems simply to be moved without changing its form by the influence of an impurity in the conductor. This may to a certain extent be regarded as supporting Matthiessen and Vogt's formula at lower temperatures.

It seemed to be of high importance that an investigation should be made as to whether their results hold good in general.

## § 3. *The alloys investigated.*

The alloys of gold with a small quantity of silver were again kindly supplied by Dr. Hoitsema. After being drawn by Heraeus to wires of 0.1 mm. diam. they were annealed together and wound round glass cylinders. After this their resistances at different temperatures were measured together in the same bath. When this was done, Dr. Hoitsema made a second analysis of

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1) A. Matthiessen. Pogg. Ann. 122 (1861) p. 353.

2) J. A. Fleming. Proc. Roy. Inst. 1896. p. 9.

each, for the results of my measurements did not agree with the amounts of silver given by the first analysis. The second analysis showed that the amounts of admixtures were not the same as before. They were:

TABLE I. Composition of the gold-silver alloys.

| | Total admixture in perc. | Silver. | Iron. |
|---|---|---|---|
| No. I | 0.396 | 0.14 | 0.08 |
| „ II | 0.476 | — | — |
| „ III | 0.524 | — | — |
| „ IV | 0.868 | 0.65 | 0.09 |
| „ V | 1.402 | — | — |

The presence of iron is probably caused by the operation of drawing the wires. The further admixture, other than silver, must be attributed to impurity in the original material. The numbers given above in addition to the results given in previous Communications, particulary in No. 99c, prove, however, that during the drawing great care must be taken to keep the material pure for instance by cleaning the wire with acids each time it is drawn.

## § 4. *The results of the observations.*

To facilitate comparison, the resistances have been expressed in that at 0° C. as unit. The resistance of all wires at 0° C. was about 9 $\Omega$. Besides these five alloys two others with greater percentages of silver were afterwards investigated. The results of these observations are given in table II.

TABLE II. Resistances of gold-silver alloys.
Change with temperature.

| Temperature | No. I.<br>0.396°/$_0$ | No. II.<br>0.476°/$_0$ | No. III<br>0.524°/$_0$ | No. IV.<br>0.868°/$_0$ | No. V.<br>1.402°/$_0$ | No. VI.<br>20.037°/$_0$ | No. VII<br>47.985°/$_0$ 2) |
|---|---|---|---|---|---|---|---|
| 0° | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 0° 1) | 1.00007 | 1.00049 | 1.00022 | 1.00026 | 1.00009 | — | — |
| — 103.83 | 0.64549 | 0.65001 | 0.65303 | 0.68497 | 0.71427 | 0.91304 | 0.91946 |
| — 139.87 | 0.52204 | 0.52794 | 0.53184 | 0.59588 | 0.61458 | — | — |
| — 182.75 | 0.37189 | — | — | 0.44014 | — | — | — |
| — 182.75 | 0.37189 | 0.37920 | 0.38483 | 0.44031 | 0.49260 | — | — |
| — 183.00 | — | — | — | — | — | 0.84304 | 0.86951 |
| — 183.57 | 0.36890 | 0.37629 | 0.38194 | 0.43774 | 0.49028 | — | — |
| — 195.17 | 0.32771 | 0.33536 | 0.34147 | 0.40226 | 0.45638 | — | — |
| — 197.87 | — | — | — | — | — | 0.82902 | 0.85850 |
| — 204.67 | 0.29295 | 0.30111 | 0.30766 | 0.36864 | 0.42821 | — | — |
| — 205.01 | — | — | — | — | — | 0.82280 | 0.85319 |
| — 215.34 | — | — | — | — | — | 0.81288 | 0.84508 |
| — 216.91 | 0.24826 | 0.25674 | 0.26359 | 0.32934 | 0.39136 | — | — |
| — 252.92 | 0.13949 | 0 14858 | 0.15584 | 0.22983 | 0.29904 | 0.78406 | 0.82196 |
| — 255.13 | — | — | — | — | — | 0.78252 | — |
| — 258.81 | — | — | — | — | — | 0.78052 | 0.82091 |
| — 259.22 | 0.13252 | 0.14170 | 0.14885 | 0.22205 | 0.29299 | — | — |
| — 261.— | — | — | — | — | — | 0.78126 | — |

Alloys No. VI and VII also were analysed before being drawn (cf. § 3); before, No. VI was found to contain 20.050°/$_0$ silver and No. VII 48.020°/$_0$ silver.

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1) After the measurements at low temperatures.

2) Results of analysis after drawing.

Though the percentages of these two have thus changed a little, the change is much smaller than that of the five other alloys, probably owing to the fact that in this case the wires were cleaned with acids each time they were drawn.

An alloy containing 79.986°/$_0$ silver was also supplied by Dr. Hoitsema and drawn by Heraeus; this wire, however, was so very brittle that it always broke in different places after winding.

### § 5. *Representation by formulae.*

To ascertain any regularity in the change of the resistance of the alloys with temperature, I calculated the specific resistance [1]) at 0°C. of the alloys (col. 2 table III) according to a formula of Liebenow [2]) representing Matthiessen's observations.

Further, if we imagine how the two metals can be arranged in the alloy we see that there are two extreme possibilities. The particles of the metals can be situated behind each other or alongside each other; from the former supposition would result

TABLE III. Specific resistances at 0°C. of gold-silver alloys.

| $x$ Volume of silver. | Calculated according to Matthiessen's observations. | $(1-x)\,W_{Au}+x\,W_{Ag}$ | $\frac{W_{Au}\;W_{Ag}}{(1-x)\,W_{Ag}+x\,W_{Au}}$ |
|---|---|---|---|
| No. I 0.00726 | 0.023713 | 0.021393 | 0.021377 |
| „ II 0.00872 | 0.024167 | 0.021385 | 0.021366 |
| „ III 0.00960 | 0.024449 | 0.021380 | 0.021360 |
| „ IV 0.01586 | 0.026371 | 0.021344 | 0.021309 |
| „ V 0.02550 | 0.029302 | 0.021288 | 0.021234 |

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1) Throughout this paper "specific resistance" is used to indicate the resistance of a wire 1 m. long and 1 mm.$^2$ section.

2) C. Liebenow. Z. S. für Electrochemie 4 (1897) p. 210; Der elektrische Widerstand der Metalle, Halle 1898 p 32.

that the resistance of the alloy is the sum of the partial resistances of the components; from the latter, that the conductivity is the sum of the partial conductivities. Most probably the real case lies between these two extremes. Taking the specific resistances ($W$.) at 0°C of gold and silver $W = 0.021436$ and $W = 0.015623$ we obtain in the first case the results given in col. 3, and in the second, those of col. 4.

In this table and throughout this paper $x$ refers to silver and therefore $1 - x$ to gold.

It appears that the two arrangements give a very small difference in resistance, but that the difference between calculated and real resistance is of a higher order ofmagnitude.

From the specific resistances at 0°C., calculated according to Matthiessen's observations I have deduced by means of the observed change with temperature (table II), the resistances at — 103°, — 182°, and — 252°C. They are given in col. 2 table IV.

Further, I have calculated the specific resistances at these temperatures on the assumption that they depend upon the conductivities of the components gold and silver according to their volume-percentage (formula col. 4 table III).

They are given in col. 3 table IV. The difference between these two series of resistances we call "additive resistance"; its values are given in col. 4.

TABEL IV. Specific resistances of gold-silver alloys.
Change with temperature.

| Temperature. | Specific resistance. | Calculated specific resistance. | Additive resistance. | Mean add. resistance. | Mean add. resist. for 1% (vol) silver. |
|---|---|---|---|---|---|
| N°. I. | | Vol. Silver 0.00726 | | | |
| 0° | 0.023713 | 0.021377 | 0.0023360 | 0.00272 | 0.00374 |
| — 103.83 | 0.0153070 | 0.0126761 | 0.0026309 | | |
| — 182.73 | 0.0088186 | 0.0058099 | 0.0030087 | | |
| — 252.92 | 0.0030770 | 0.0001745 | 0.0029025 | | |

| Temperature. | Specific resistance. | Calculated specific resistance. | Additive resistance. | Mean add. resistance. | Mean add. resist. for 1% (vol.) silver. |
|---|---|---|---|---|---|
| Nº. II. | | Vol. Silver 0.00872 | | | |
| 0° | 0.024167 | 0.021366 | 0.0028010 | 0.00315 | 0.00361 |
| — 103.83 | 0.0157090 | 0.0126685 | 0.0030405 | | |
| — 182.73 | 0.0091641 | 0.0058058 | 0.0033583 | | |
| — 252.92 | 0.0035907 | 0.0001745 | 0.0034162 | | |
| Nº. III. | | Vol. Silver 0.00960 | | | |
| 0° | 0.024441 | 0.021360 | 0.0030810 | 0.00340 | 0.00353 |
| — 103.83 | 0.0159610 | 0.0126642 | 0.0032968 | | |
| — 182.73 | 0.0094056 | 0.0058031 | 0.0036025 | | |
| — 252.92 | 0.0038089 | 0.0001744 | 0.0036345 | | |
| Nº. IV. | | Vol. Silver 0.01586 | | | |
| 0° | 0.026371 | 0.021309 | 0.0050620 | 0.00555 | 0.00350 |
| — 103.83 | 0.0180630 | 0.0126326 | 0.0054304 | | |
| — 182.73 | 0.0116110 | 0.0057855 | 0.0058255 | | |
| — 252.92 | 0.0060609 | 0.0001742 | 0.0058867 | | |
| Nº. V. | | Vol. Silver 0.02550 | | | |
| 0° | 0.029302 | 0.021234 | 0.0080680 | 0.00842 | 0.00330 |
| — 103.83 | 0.0209300 | 0.0125842 | 0.0083458 | | |
| — 182.73 | 0.0144340 | 0.0057585 | 0.0086755 | | |
| — 252.92 | 0.0087625 | 0.0001736 | 0.0085889 | | |
| Nº. VI. | | Vol. Silver 0.31557 | | | |
| 0° | 0.0919780 | 0.0191835 | 0.0727945 | 0.0725 | |
| — 103.83 | 0.0839796 | 0.0112853 | 0.0726943 | | |
| — 182.73 | 0.0775632 | 0.0050487 | 0:0725145 | | |
| — 252.92 | 0.0721190 | 0.0001618 | 0.0719572 | | |
| Nº. VII. | | Vol. Silver 0.62928 | | | |
| 0° | 0.0993780 | 0.0173691 | 0.0820089 | 0.0817 | |
| — 103.83 | 0.0913740 | 0.0101520 | 0.0812220 | | |
| — 182.73 | 0.0864260 | 0.0044547 | 0.0819713 | | |
| — 252.92 | 0.0816857 | 0.0001504 | 0.0815353 | | |

The chief conclusion to which this table leads is, that the additive resistance changes very slightly with temperature. In the case of the first five alloys the additive resistance seems to increase somewhat at lower temperatures, whereas in the last it decreases a little. As a first approximation we may suppose that it is constant.

A second important conclusion may be drawn from table IV. If we take the mean of the additive resistance at different temperatures (cf. col. 5), this mean proves to be proportional to the percentage of the volume of silver (cf. col. 6). The factor of proportionality for the different percentages does not differ more than 3 % from the mean; hence we find for a wire, 1 m. long and 1 mm.$^2$ in section, of an alloy with 1 % silver, an additive resistance of 0.00360 $\Omega$.

This proportionality, however, holds only for small quantities of admixtures and not for alloys VI and VII. For larger amounts another relation must exist, as follows from MATTHIESSEN's observations. LIEBENOW [1]) from this theory of electrical resistance, which will be discussed more completely in another section, has deduced a formula in which the additive resistance is given by

$$\frac{x(1-x)\mu}{a(1-x)+bx}.$$

Here $\mu$ is a constant connected, according to LIEBENOW, with the thermoelectric power of gold-silver, and $a$ and $b$ are proportional to the internal molecular heat-conductivities of these metals. To make this formula agree with the observations of MATTHIESSEN, LIEBENOW puts $\frac{b}{a} = 1.14444$. Since, however, this value for $\frac{b}{a}$ is much smaller than the ratio of the molecular heat-conductivities given by the experiments of JAEGER and DIESSELHORST [2]), viz. 1.4285, the coefficients $a$ and $b$ have not the signification for which they were introduced in LIEBENOW's theory.

For $\mu$ the same remark may be made (cf. § 9).

As, therefore, the basis underlying LIEBENOW's formula proves to be unsound, I for simplicity calculated a quadratic formula to express the additive resistance as a function of the composition. I will accept provisionally that the additive resistance at low temperatures is expressed by the same formula as that at 0° C. This formula [3]) is:

$$A_x = -0.0011104(1-x) + 0.0015736\,x + 0.344059\,x(1-x),$$

---

1) C. LIEBENOW: Der electrische Widerstand der Metalle, Halle, 1898, and Zeits. f. Electroch. 4. p. 2016 (1897).

2) JAEGER and DIESSELHORST Abh. Phys. Tech. Reichsanst. 1900.

3) The formula given here supersedes that of p. 67 of my Thesis, which — as was kindly remarked by Dr. KEESOM — was written there erroneously.

in which $x$ refers to the volume of silver and $(1-x)$ to that of gold. In cols. 2 and 3 respectively of Table V are given the values which LIEBENOW calculated from MATTHIESSEN's observations for the specific resistance observed at 0°C. and for the resistance that would follow from the volume composition of the alloys according to the simple law of mixtures. Col. 4 gives their differences, which we have called the additive resistances. Col. 5 gives the difference between the additive resistance of col. 4 (0) and the value which I calculated for it with the above mentioned formula for $A$ (C).

TABLE V. Resistance of gold-silver alloys at 0°C. according to MATTHIESSEN's observations. Length 1 Meter, section 1 mm$^2$.

| Vol. % of gold. | Specific resistance. | Res. calculated from vol. % according to simple law of mixtures. | Additive resistance. | 0—C. |
|---|---|---|---|---|
| 98.81 | 0.0243 | 0.02132 | + 0.00298 | + 0.00003 |
| 98.23 | 0.0271 | 0.02128 | 0.00582 | + 90 |
| 97.27 | 0.0298 | 0.02121 | 0.00859 | + 50 |
| 94.07 | 0.0388 | 0.02096 | 0.01784 | — 40 |
| 88.80 | 0.0524 | 0.02057 | 0.03183 | + 157 |
| 85.61 | 0.0608 | 0.02033 | 0.04047 | — 120 |
| 79.86 | 0.0731 | 0.01993 | 0.05317 | — 160 |
| 66.47 | 0.0948 | 0.01905 | 0.07575 | — 71 |
| 49.79 | 0.1055 | 0.01805 | 0.08745 | + 120 |
| 33.14 | 0.0945 | 0.01716 | 0.07734 | + 42 |
| 19.86 | 0.0733 | 0.01651 | 0.05679 | + 97 |
| 14.18 | 0.0605 | 0.01625 | 0.04425 | + 119 |
| 11.02 | 0.0511 | 0.01610 | 0.03500 | — 1 |
| 5.84 | 0.0366 | 0.01587 | 0.02073 | + 38 |
| 2.68 | 0.0261 | 0.01574 | 0.01036 | — 11 |
| 1.74 | 0.0243 | 0.01569 | 0.00861 | + 120 |
| 1.14 | 0.0198 | 0.01567 | 0.00431 | — 128 |

I now pass to the formulae necessary to express the resistances of my alloys as a function of the temperature, and to the discussion of the degree of accuracy with which these formulae can represent experimental results. I derived for them the coefficients of formulae of the same type as those given for pure metals (cf. Comm. No. 95*b*) and made them agree as well as possible with experiment in the same manner as before. The formula chosen had the form :

$$\frac{W_t}{W_0} = 1 + a\frac{t}{100} + b\left(\frac{t}{100}\right)^2 + c\left(\frac{t}{100}\right)^3 +$$
$$+ e\left(\frac{10^6}{T^3} - \frac{10^6}{(273.09)^3}\right) + f\left(\frac{10^{10}}{T^5} - \frac{10^{10}}{(273.09)^5}\right).$$

The calculated coefficients are given in table VI and the differences between calculations and observations in col. 3 of table VII.

**TABLE VI. First calculation of coefficients for the formula (D)**

| Alloy Vol. silver. | $a$ | $b$ | $c$ | $e$ | $f$ |
|---|---|---|---|---|---|
| N°. I 0.726°/o | $+ 0.343244$ | $+0.0060958$ | $+0.0036190$ | $+0.0_3317520$ | $-0.0_5383646$ |
| N°. II 0.872°/o | $+ 0.336487$ | $+0.0032529$ | $+0.0028824$ | $+0.0_3294963$ | $-0.0_5350303$ |
| N°. III 0.960°/o | $+ 0.332432$ | $+0.0012442$ | $+0.0020925$ | $+0.0_3258365$ | $-0.0_5298449$ |
| N°. IV 1.586°/o | $+ 0.303376$ | $+0.0042029$ | $+0.0033735$ | $+0.0_3293421$ | $-0.0_5364268$ |
| N°. V 2.550°/° | $+ 0.274025$ | $+0.0023810$ | $+0.0025103$ | $+0.0_3198459$ | $-0.0_5222440$ |
| N°. VI 31.557°/o | $+ 0.086427$ | $+0.0039805$ | $+0.0020020$ | $+0.0_3103708$ | $-0.0_5134335$ |
| N°. VII 62.928°/o | $+ 0.106085$ | $+0.037466$ | $+0.0101245$ | $+0.0_3178426$ | $-0.0_5244843$ |

TABLE VII. Resistances of gold-silver alloys. Comparison between observation and calculation.

| Temperature | Observed resistance. | 0—C (first calc.) | 0—C (1st general sol.) | 0—C (2nd general sol.) |
|---|---|---|---|---|
| Alloy No. I 0.726 °/₀ | | | | |
| 0° | 1. | 0 | 0 | 0 |
| — 103.83 | 0.64549 | $-0.0_{3}67$ | $-0.0_{3}87$ | $-0.0_{4}2$ |
| — 139.87 | 0.52204 | 0 | $+0.0_{3}37$ | $+0.0_{2}152$ |
| — 182.73 | 0.37189 | $+0.0_{3}42$ | $+0.0_{2}154$ | $+0.0_{2}304$ |
| — 183.55 | 0.36890 | $+0.0_{3}35$ | $+0.0_{2}150$ | $+0.0_{2}300$ |
| — 195.17 | 0.32771 | $+0.0_{3}66$ | $+0.0_{2}202$ | $+0.0_{2}362$ |
| — 204.67 | 0.29295 | 0 | $+0.0_{2}152$ | $+0.0_{2}320$ |
| — 216.91 | 0.24826 | $-0.0_{3}67$ | $+0.0_{2}108$ | $+0.0_{2}287$ |
| — 252.92 | 0.13949 | 0 | $+0.0_{2}458$ | $+0.0_{2}666$ |
| — 259.22 | 0.13252 | 0 | $+0.0_{2}821$ | + 0.01034 |
| Alloy No II 0.872 °/₀ | | | | |
| + 98.30 | 1.33663 | $-0.0_{4}2$ | $+0.0_{3}85$ | $-0.0_{2}195$ |
| 0° | 1. | 0 | 0 | 0 |
| — 103.83 | 0.65001 | $-0.0_{3}94$ | $-0.0_{2}258$ | $+0.0_{3}41$ |
| — 139.87 | 0.52794 | 0 | $-0.0_{2}216$ | $+0.0_{2}183$ |
| — 182.73 | 0.37920 | $+0.0_{3}41$ | $-0.0_{2}222$ | $+0.0_{2}300$ |
| — 183.55 | 0.37629 | $+0.0_{3}39$ | $-0.0_{2}223$ | $+0.0_{2}302$ |
| — 195.17 | 0.33536 | $+0.0_{3}52$ | $-0.0_{2}223$ | $+0.0_{2}339$ |
| — 204.67 | 0.30111 | 0 | $-0\ 0_{2}277$ | $+0.0_{2}308$ |
| — 216.91 | 0.25674 | $-0.0_{3}83$ | $-0.0_{2}364$ | $+0.0_{2}256$ |
| — 252.92 | 0.14858 | 0 | $-0.0_{2}156$ | $+0.0_{2}566$ |
| — 259.22 | 0.14170 | 0 | $-0.0_{2}210$ | $+0.0_{2}950$ |
| Alloy No. III. 0.960 °/₀ | | | | |
| 0° | 1. | 0 | 0 | 0 |
| — 103.83 | 0.65303 | $-0.0_{3}85$ | $-0.0_{2}306$ | $+0.0_{3}31$ |
| — 139.87 | 0.53184 | 0 | $-0.0_{2}300$ | $+0.0_{2}154$ |
| — 182.73 | 0.38483 | $+0.0_{3}58$ | $-0.0_{2}281$ | $+0.0_{2}312$ |
| — 183.55 | 0.38194 | $+0.0_{3}54$ | $-0.0_{2}287$ | $+0.0_{2}308$ |
| — 195.17 | 0.34147 | $+0.0_{3}54$ | $-0.0_{2}281$ | $+0.0_{2}352$ |
| — 204.67 | 0.30766 | 0 | $-0.0_{2}327$ | $+0.0_{2}337$ |
| — 216.91 | 0.26359 | $-0.0_{2}123$ | $-0.0_{2}431$ | $+0.0_{2}274$ |
| — 252.92 | 0.15584 | 0 | $-0.0_{2}287$ | $+0.0_{2}534$ |
| — 259.22 | 0.14885 | 0 | $+0.0_{3}56$ | $+0.0_{2}900$ |

| Temperature | Observed resistance. | 0—C (first calc.) | 0—C (1st general sol.) | 0—C (2nd general sol.) |
|---|---|---|---|---|
| Alloy No. IV 1.586 % | | | | |
| + 100.34 | 1.31205 | 0 | $-0.0_{3}12$ | $-0.0_{2}876$ |
| 0° | 1. | 0 | 0 | 0 |
| — 103.83 | 0.68497 | $-0.0_{3}85$ | $+0.0_{2}121$ | $+0.0_{2}104$ |
| — 139.87 | 0.59588 | 0 | $+0.0_{2}252$ | $+0.0_{2}227$ |
| — 182.73 | 0.44014 | $+0.0_{3}83$ | $+0.0_{2}339$ | $+0.0_{2}306$ |
| — 183.55 | 0.43774 | $+0.0_{3}89$ | $+0.0_{2}343$ | $+0.0_{2}310$ |
| — 195.17 | 0.40226 | $+0.0_{2}283$ | $+0.0_{2}528$ | $+0.0_{2}485$ |
| — 204.67 | 0.36864 | 0 | $+0.0_{2}231$ | $+0.0_{2}195$ |
| — 216.91 | 0.32934 | $+0.0_{3}48$ | $+0.0_{2}258$ | $+0.0_{2}220$ |
| — 252.92 | 0.92983 | 0 | $+0.0_{2}347$ | $+0.0_{2}300$ |
| — 259.22 | 0.22205 | 0 | $+0.0_{2}526$ | $+0.0_{2}480$ |
| Alloy No. V 2.550 °/₀ | | | | |
| + 99.33 | 1.27699 | 0 | $-0.0_{2}185$ | $-0.0_{2}312$ |
| 0° | 1. | 0 | 0 | 0 |
| — 103.83 | 0.71427 | $-0.0_{2}100$ | $-0.0_{3}27$ | $+0.0_{2}104$ |
| — 139.87 | 0.61458 | 0 | $+0.0_{3}67$ | $+0.0_{2}247$ |
| — 182.73 | 0.49260 | $+0.0_{3}42$ | $+0.0_{3}85$ | $+0.0_{2}318$ |
| — 183.55 | 0.49028 | $+0.0_{3}50$ | $+0.0_{3}93$ | $+0.0_{2}326$ |
| — 195.17 | 0.45638 | $+0.0_{3}39$ | $+0.0_{3}67$ | $+0.0_{2}316$ |
| — 204.67 | 0.42821 | 0 | $+0.0_{3}17$ | $+0.0_{2}277$ |
| — 216.91 | 0.39136 | $-0.0_{3}93$ | $-0.0_{3}94$ | $+0.0_{2}181$ |
| — 252.92 | 0.29904 | 0 | $-0.0_{2}264$ | $+0.0_{3}58$ |
| — 259.22 | 0.29299 | 0 | $-0.0_{4}6$ | $+0.0_{2}322$ |
| Alloy No. VI 31.557 °/₀ | | | | |
| 0° | 1. | 0 | 0 | 0 |
| — 102.99 | 0.91304 | 0 | $-0.0_{2}422$ | $+0.0_{3}69$ |
| — 183.00 | 0.84304 | 0 | $-0.0_{2}821$ | $+0.0_{2}54$ |
| — 197.87 | 0.82902 | $-0.0_{3}29$ | $-0.0_{2}963$ | $-0.0_{3}17$ |
| — 205.01 | 0.82280 | $+0.0_{3}12$ | $-0.0_{2}973$ | $+0.0_{4}6$ |
| — 215.34 | 0.81288 | 0 | —0.01086 | $-0.0_{3}58$ |
| — 252 93 | 0.78406 | 0 | —0.01283 | $-0.0_{3}73$ |
| — 255.13 | 0.78252 | $-0.0_{3}35$ | —0.01285 | $-0.0_{3}66$ |
| — 258.11 | 0.78052 | 0 | —0.01264 | $-0.0_{3}27$ |
| [— 261.—] | 0.78126 | $+0.0_{2}792$ | | |

| Temperature | Observed resistance. | 0—C (first calc.) | 0—C (1st general sol.) | 0—C (2nd general sol.) |
|---|---|---|---|---|
| Alloy No. VII 62.928 % | | | | |
| 0° | 1. | 0 | 0 | 0 |
| — 102.99 | 0.92651 | 0 | — 0.01130 | — 0.00817 |
| — 183.00 | 0.87620 | — 0.00025 | — 0.00586 | — 0.00029 |
| — 197.87 | 0.86510 | — 10 | — 0.00633 | — 0.00029 |
| — 205.01 | 0.85974 | 0 | — 0.00656 | — 0.00031 |
| — 215.34 | 0.85157 | 0 | — 0.00739 | — 0.00072 |
| — 252.93 | 0.82828 | 0 | — 0.00709 | + 0.00062 |
| — 258.81 | 0.92723 | 0 | — 0.00642 | + 0.00148 |

If we suppose now that in the formula

$$W_t = W'_t + A,$$

where $W_t$ is the observed resistance at temperature $t$, and $W'_t$ is the corresponding resistance calculated from the conductivities of the components according to the ratio of their volumes (cf. table IV col. 3), the additive resistance $A$ is independent of temperature, that

$$W'_t = W'_0 \left\{ 1 + a'\, t + b'\, t^2 + c'\, t^3 + e' \left( \frac{10^6}{T^3} - \frac{10^6}{(273.09)^3} \right) + \right.$$
$$\left. + f' \left( \frac{10^{10}}{T^5} - \frac{10^{10}}{(273.09)^5} \right) \right\}$$

and that $a'$, $b'$ etc. are equal to the same coefficients for pure gold: $a' = a_{Au}$, $b' = b_{Au}$ etc, then we find

$$W'_0 \left\{ 1 + a'\, t + b'\, t^2 + c'\, t^3 + e' \left( \frac{10^6}{T^3} - \frac{10^6}{(273.09)^3} \right) + \right.$$
$$\left. + f' \left( \frac{10^{10}}{T^5} - \frac{10^{10}}{(273.09)^5} \right) \right\} + A = W_0 \left\{ 1 + a\, t + b\, t^2 + c\, t^3 + \right.$$
$$\left. + e \left( \frac{10^6}{T^3} - \frac{10^6}{(273.09)^3} \right) + f \left( \frac{10^{10}}{T^5} - \frac{10^{10}}{(273.09)^5} \right) \right\}$$

Hence it follows $W'_0\, a' = W_0\, a$

$$W'_0\, b' = W_0\, b, \text{ etc.}$$

For the various alloys, distinguished here as in the former tables by Roman figures, we thus obtain

$$\frac{W_{I0}}{W'_{I0}}\,a_I = \frac{W_{II0}}{W'_{II0}}\,a_{II} = \text{etc.} = a'$$

$$\frac{W_{I0}}{W'_{I0}}\,b_I = \frac{W_{II0}}{W'_{II0}}\,b_{II} = \text{etc.} = b'.$$

From the coefficients of table VI the values of $a'$, $b'$, $c'$, $e'$, and $f'$ have been separately calculated for each alloy. On account of the larger deviation found for the alloy VII for the original coefficient $a$, this result has been omitted in calculating the mean $a'$, etc. From the mean of the constants $a'$ etc., $a$, $b$, $c$, $e$, and $f$ have again been derived for the different alloys. A further adjustment has been made according to the method of Dr. E. F. VAN DE SANDE BAKHUYZEN, and so were obtained the coefficients given in table VIII.

TABLE VIII. Coefficients 1st general solution.

| | *a* | *b* | *c* | *e* | *f* |
|---|---|---|---|---|---|
| Alloy No I | +0.345399 | +0.0036671 | +0.0031174 | +0.0002915 | —0.00000365521 |
| II | +0.339323 | +0.0036026 | +0.0030625 | +0.0002863 | —0.00000359107 |
| III | +0.335883 | +0.0035661 | +0.0030315 | +0.0002834 | —0.00000355466 |
| IV | +0.308897 | +0.0032796 | +0.0027879 | +0.0002607 | —0.00000326899 |
| V | +0.278798 | +0.0029600 | +0.0025162 | +0.0002352 | —0.0000295040 |
| VI | +0.081475 | +0.0008649 | +0.0007353 | +0.0000687 | —0.0000086218 |
| VII | +0.068269 | +0.0007247 | +0.0006161 | +0.0000576 | —0.00000072233 |

By means of these coefficients the resistances for all temperatures have again been calculated. The results of these calculations have been given in col. 4 of table VII.

For the adjustment after the method of VAN DE SANDE BAKHUIJZEN conducing to table VIII, only the alloys Nos. I—V have been considered. This with the omission of alloy No VII in calculating the mean $a'$ etc., are the reasons why the calculations for the alloys VI and VII do not fit the observations as well as those for alloys Nos. I—V.

If we consider the great influence of very small amounts of admixtures and the comparative insufficiency of our knowledge of the compositions of the alloys containing small amounts of silver, we may be highly satisfied with the agreement between formula and observations, especially with the first five alloys. Hence we may conclude, that the resistances of alloys of gold and silver of different compositions over the whole region of low temperatures, can be represented by such a general formula. In the case of the alloys with larger amounts of silver we can diminish the differences yet remaining between observed and calculated values by considering the coefficients of $W'$ not as constants, but as functions of the composition. This supposition is obvious, for pure gold and silver have already different coefficients and the coefficients $a'$, $b'$, etc. of their alloys will differ a little from those of the pure metals and also from each other. For simplification we have supposed that only the first coefficient, $a'$ will depend upon the composition. A quadratic function of the composition has been supposed, viz:

$$a' = \alpha x + \beta (1-x) + \gamma x (1-x)$$

where $\alpha = 0.348728$ ; $\beta = 0.377017$ ; $\gamma = 0.188017$.

The coefficients $a$ for the different alloys calculated from the values of $a'$ resulting from this formula are given in table IX.

TABLE IX. Coefficient $a$, 2nd general solution.

| Alloy I | II | III | IV | V | VI | VII |
|---|---|---|---|---|---|---|
| 0.341901 | 0.337944 | 0.334940 | 0.304841 | 0.276594 | 0.085241 | 0.070449 |

Col. 5 table VII gives the differences of the observed specific resistances and the specific resistances calculated by means of these values of $a$ and those of $b$, $c$, $e$, $f$ from table VII.

§ 6. *The general formula for the resistance of equal wires of alloys of gold and silver of all compositions and at all temperatures.*

Résumé of the general formula:

$$W_{xt} = \frac{W_{\mathrm{Au}}\,W_{\mathrm{Ag}}}{W_{\mathrm{Ag}}(1-x)+W_{\mathrm{Au}}\,x}\left\{1 + a'\left(\frac{t}{100}\right) + b'\left(\frac{t}{100}\right)^2 + c'\left(\frac{t}{100}\right)^3 + \right.$$
$$\left. + e'\left(\frac{10^6}{T^3} - \frac{10^6}{(273.09)^3}\right) + f'\left(\frac{10^{10}}{T^5} - \frac{10^{10}}{(273.09)^5}\right)\right\} + Ax + B(1-x) +$$
$$+ Cx\,(1-x).$$

The values of the constants in this formula are for a wire of 1 m. long and 1 mm² section: $W_{\mathrm{Au}} = 0.021436\ \Omega$,
$W_{\mathrm{Ag}} = 0.015628\ \Omega$

and (1st general solution):

| $a'$ | $b'$ | $c'$ | $e'$ | $f'$ |
|---|---|---|---|---|
| +0.395203 | +0.0031715 | +0.0030424 | +0.00041938 | −0.00000513494 |

| $A$ | $B$ | $C$ |
|---|---|---|
| 0.0015736 | — 0.0011104 | 0.344059 |

Finally, in order to get a somewhat better adjustment we can put (2nd general solution): $a' = \alpha x + \beta\,(1-x) + \gamma\, x\,(1-x)$

| $\alpha$ | $\beta$ | $\gamma$ |
|---|---|---|
| 0.348728 | 0.377017 | 0.188017 |

The mean error of the 2nd general solution for the alloys I to V is 0.0042 Ω corresponding with 1°.1, for alloy V 0.00074 Ω or 0.9°, and for alloy VII 0.00106 Ω or 1.2°. In calculating this mean error the error at —259° is left out of account.

If we calculate the resistance of pure gold by putting $x = 0$ in the general formula which has been deduced for gold-silver alloys, we obtain values at low temperatures greater than those observed (cf. Comm. N⁰. 107*b*). Thus the decrease in the resistance of the gold wire $Au_V$ at low temperatures is greater than that which we would calculate by putting $x = 0$ in the general formula; this might by explained by the supposition that the values for $x$ given by analysis are too small, which indeed, seems to be the case. On the other hand, the decrease in the resistance of $Au_0$ at low temperatures, the data of which were given in Comm. N⁰. 99*c*, and the impurity of which was found to be 0.03 %, was less than that of an imaginary wire whose resistance was calculated from the general formula by extrapolation to $x = 0$. The values of the observed resistances, and the differences between observation and calculation have already been published in Comm. N⁰. 107*c*, table I, cols. 2 and 5, and the extrapolated coefficients in the last line of table II of the same communication.

### § 7. *Results, and diagram.*

A survey of the change of the resistance with temperature is given by the diagram (Plate I) referring not only to the alloys of gold and silver but also to the pure metals and two kinds of impure gold. Values of $\frac{T}{273.09} - \frac{W_t}{W_0}$ are plotted as ordinates and temperatures as abscissae. This ordinate indicates therefore the difference between the observed resistance and the resistance that we calculate starting from 0°C. and supposing that the change is proportional to the absolute temperature.

The diagram shows that the change of the resistance with temperature of alloys of gold and silver of different compositions is very regular. For all the alloys a point of inflexion appears in the curve at nearly the same temperature; after this all the curves bend quickly downwards. It is further proved, that theoretically, there must be one alloy, of which the resistance from 0° to about — 200°C. is proportional to the absolute temperature. If it were practicable to make such an alloy, this would be most suitable for thermometrical determinations.

### § 8. *Theories concerning the resistance of alloys.*

By means of the preceding data we are now able to test the theory of Rayleigh and Liebenow in the case of alloys of gold and silver. Rayleigh in 1896 ¹) formed the hypothesis that the

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¹) Rayleigh Scientific Papers IV p. 232. Nature 54 p. 154.

amount by which the electrical resistance of an alloy of two metals is greater than that calculated from the volume-composition by the simple law of mixtures may be due to a thermoelectric origin. He imagines the two metals in the alloy arranged in very thin layers, one behind the other, so that when an electric current flows through these layers, a Peltier-effect will occur, heating the point of contact of the metals 1 and 2 and cooling that of 2 and 1. By this alternate heating and cooling a thermoelectric current, opposed to the main current, will arise, having the same effect therefore as adding a further resistance. Rayleigh computes this additive resistance by a simple method, and finds it to be at 0°C.

$$A' = \frac{273\, E^2}{k_1/x + k_2/(1-x)}$$

in which $E$ is the thermoelectric power, $k_1$ and $k_2$ are the heat-conductivities and $x$ and $1-x$ are the volume-ratios of the two components.

Liebenow follows the same idea (l. c). In his calculations, however, he introduces a false relation between the thermoelectric power and the Peltier-effect; and hence obtains a wrong result (cf. Thesis for the doctorate chapter VII). If we introduce this relation in its correct and generally valid form we find, in agreement with Rayleigh, for an arbitrary temperature on the absolute scale:

$$A' = \frac{TE^2}{k_1/x + k_2/(1-x)}$$

Since, in the preceding, it has been proved that the additive resistance has nearly the same value at all temperatures, and $k_1$ and $k_2$ change but slightly with temperature, $TE^2$ ought also to be a constant. Theoretically, however, there is no reason for expecting this.

### § 9. *Electromotive force and thermoelectric power of the couple gold-silver.*

To come to a conclusion about this question, I measured the electromotive force from + 100° down to the lowest temperatures completing the calibration at hydrogen temperatures given by Kamerlingh Onnes and myself in Comm. N⁰. 107*b*. viz. down to —259°C. of a gold-silver thermoelement made from wires drawn from the same metal as those of which the resistance was measured. An accurate investigation of the homogeneity of the wires was first made. For the electromotive force when one junction was in ice, and the other was placed in the cryostat already described, the values given in table X col. 2 including these of table I Comm. N⁰. 107*b* were found.

TABLE X.

| Temp. | Observed electromotive force in millivolts. | O — C. | Thermoelectric power. $E$ in millivolts. | $T$ | $E^2T$. |
|---|---|---|---|---|---|
| + 100 | 0.0 15 | 0 | 0.000192 | 373.09 | $0.0_{3}0137$ |
| + 70 | 0.0064 | + 0.0006 | 0.000176 | 343.09 | $0.0_{3}0106$ |
| + 56 | 0.0042 | + 0.0006 | 0.000144 | 329.09 | $0.0_{3}0068$ |
| + 26 | 0.0010 | 0.0005 | 0.000058 | 299.09 | $0.0_{3}0010$ |
| + 15.5 | 0.0006 | 0.0005 | 0.000028 | 288·59 | $0.0_{3}0002$ |
| + 6 | — | — | 0 | 279.09 | 0 |
| 0 | — | — | 0.000016 | 273.09 | $0.0_{5}0007$ |
| — 7 | 0.0004 | 0.0002 | — 0.000035 | 266.09 | $0.0_{3}0003$ |
| — 23 | 0.0010 | 0 | — 0.000074 | 250.09 | $0.0_{3}0014$ |
| — 70 5 | 0.0137 | — | — 0.000186 | 202.59 | $0.0_{3}0070$ |
| — 103.95 | 0.01528 | 0 | — 0.000312 | 169.14 | $0.0_{3}0165$ |
| — 164.04 | 0.05124 | + 0.00221 | — 0.000932 | 109.05 | $0.0_{3}0947$ |
| — 182.75 | 0.06952 | — 0.00037 | — 0.001317 | 90.34 | $0.0_{3}1569$ |
| — 195.17 | 0.08470 | — 0.0035 | — 0.001648 | 77.92 | $0.0_{3}2118$ |
| — 204.68 | 0.09872 | — 0.0066 | — 0.001948 | 68.41 | $0.0_{3}2598$ |
| — 212.82 | 0.11356 | — 0.00876 | — 0.002241 | 60.27 | $0.0_{3}3029$ |
| — 216.01 | 0.11972 | — 0.00998 | — 0.002366 | 57.08 | $0.0_{3}3195$ |
| — 252.86 | 0.24742 | — 0.0017 | — 0.004269 | 20.23 | $0.0_{3}3687$ |
| — 255.34 | 0.26304 | + 0.0031 | — 0.004432 | 17.75 | $0.0_{3}3487$ |
| — 258.61 | 0.28912 | + 0.0143 | — 0.004654 | 14.48 | $0.0_{3}3136$ |

The following formula served to express the electromotive force as a function of the temperature : $F = at + bt^2 + ct^3 + dt^4 + et^5$.

$$\begin{aligned} a &= -\ 0.0_4 16028 \\ b &= +\ 0.0_5 13463 \\ c &= +\ 0.0_8 25023 \\ d &= -\ 0.0_{11} 6682 \\ e &= -\ 0.0_{12} 21943 \end{aligned}$$

The deviations of the formula from the observed values are given in table X col. 3. To get the value of $E$, the thermoelectric power at a definite temperature, we must differentiate according to $t$ at that temperature. Therefore :

$$E = a + 2\,bt + 3\,ct^2 + 4\,dt^3 + 5\,et^4.$$

The values of $E$ at the various temperatures are given in table X col. 4. The thermoelectric power at 0°C. is very small. According to my formula, the neutral point lies in the neighbourhood of 0°C. Jaeger and Diesselhorst give for the thermoelectric power of gold-silver at 18°C. a value, that is smaller than the limit of accuracy of their observations (Wiss. Abh. der Phys. Techn. Reichsanst. 1900).

In table X col. 6 values of $E^2T$ are given. From this it appears that $E^2T$ is by no means constant ; hence, the hypothesis of Rayleigh and Liebenow, that the additive resistance is of thermoelectric origin, is not supported by my experiments. If we calculate the additive resistance for a wire 1 m. long and 1 mm.$^2$ section from Rayleigh's formula, we find for alloy N°. V at 0°C. $A' = 41.10^{-14}\ \Omega$, while experiment gave $A' = 81.10^{-4}\ \Omega$. Further at $-216$°C. calculation gives $A' = 18.10^{-9}\ \Omega$, while according to experiment $A'$ remains the same. Thus there is by no means an agreement between calculation and experiment. Hence the only existing theory that tries to explain the additive resistance of alloys, does not hold 1). The

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1) Guertler has shown (Zeitschr. f. anorg. Chem. 51, p. 397, 1906) that most probably there is a relation between the formation of mixed crystals and the existence of an additive resistance. The explanation of this relation was not suggested.

reason why LIEBENOW's calculations give correct results is that, in calculating a formula with 2 independent constants [1]) for the curve that represents MATTHIESSEN's observations he considers the resistance of alloys of different percentages only at one temperature. As already stated these calculated constants are, however, not at all in agreement with the values of the thermoelectric power of gold-silver, and the heat-conductivities of these metals, which they are supposed to represent in the formula. Another argument against that theory, is, that e. g. zinc, tin, cadmium and lead when alloyed with each other do not show an additive resistance, whereas for these metals the thermoelectric power at ordinary temperatures is larger than for gold and silver.

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1) Only the ratios of the three constants occurring in the formula of LIEBENOW can be deduced from experimental determinations of the additive resistance; they are therefore equivalent to two independent constants.

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,
*Director of the Laboratory.*

## No. 108.

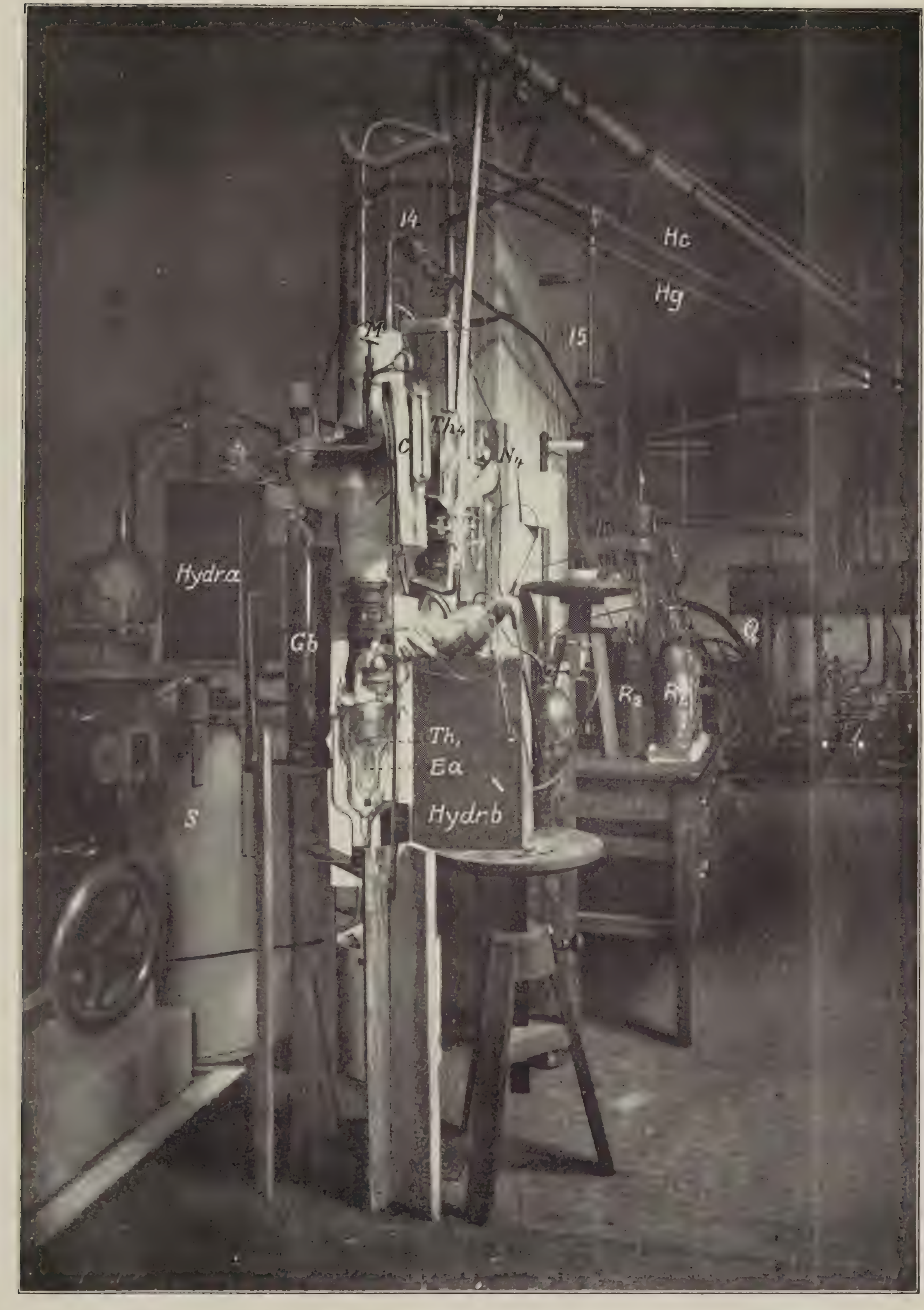
**Dr. H. KAMERLINGH ONNES**. "The liquefaction of helium." (*With three plates*).

(*Translated from: Bijvoegsel aan het Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling der Kon. Akademie van Wetenschappen te Amsterdam van* 27 Juni 1908, p 163—179, *edited* **August 7, 1908**).

EDUARD IJDO - PRINTER - LEIDEN.

**Dr. H. KAMERLINGH ONNES** **"The liquefaction of helium."**

**PLATE I.**



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**Dr. H. KAMERLINGH ONNES. "The liquefaction of helium."**

PLATE II.

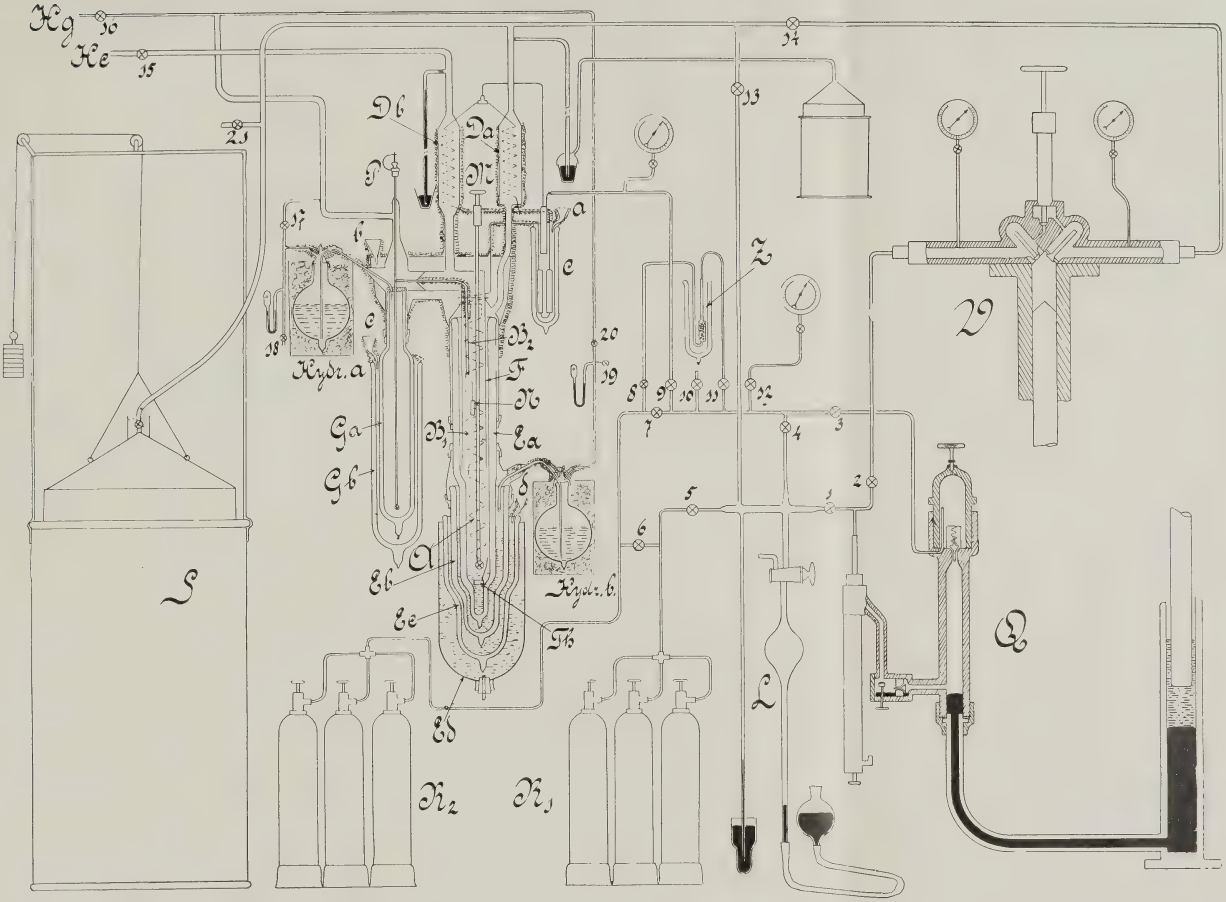

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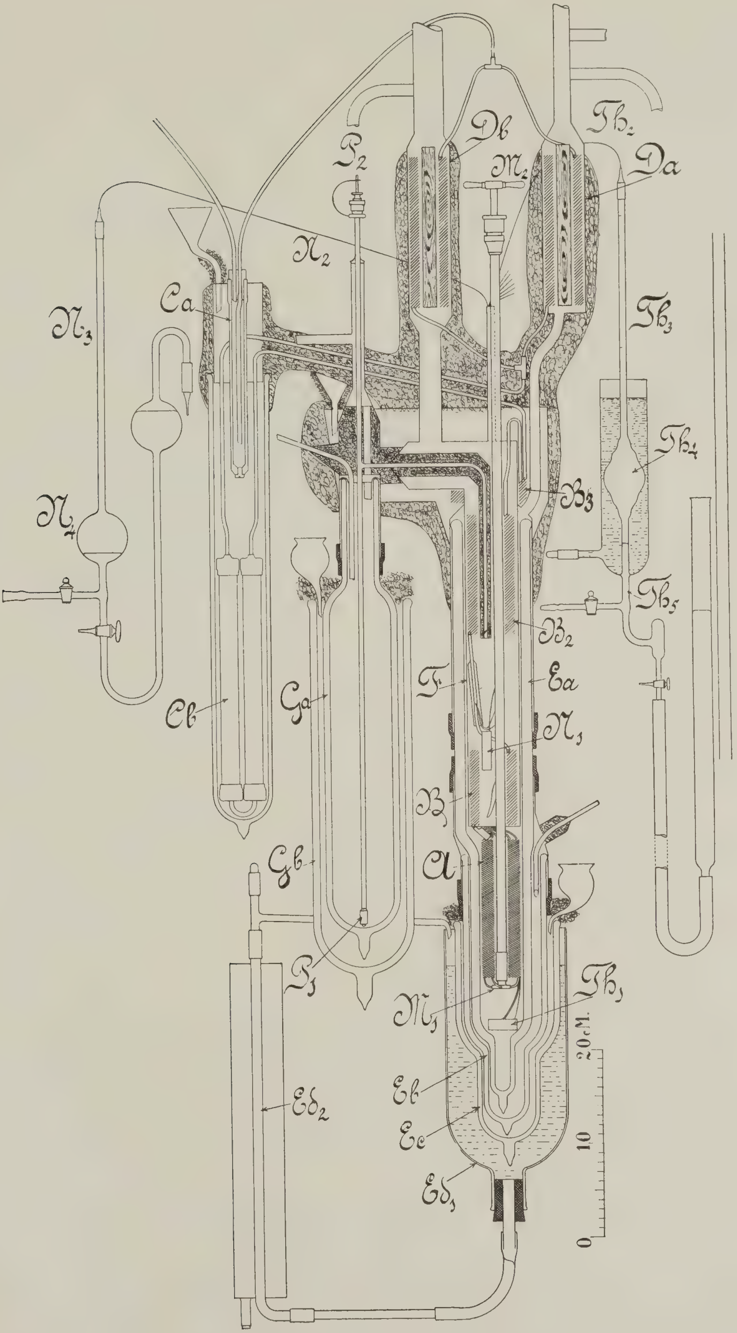
PLATE III.



Communication N°. 108

## **Dr. H. KAMERLINGH ONNES.** "*The liquefaction of helium.*"

§ 1. *Method.* As a first step on the road towards the liquefaction of helium the theory of VAN DER WAALS indicated the determination of its isotherms, particularly for the temperatures which are to be attained by means of liquid hydrogen. From the isotherms the critical quantities may be calculated, as VAN DER WAALS did in his Thesis for the Doctorate among others for the permanent gases of FARADAY, which had not yet been made liquid then, either by first determining *a* and *b*, or by applying the law of the corresponding states. Led by the considerations of Comm. N^0^. 23 (Jan. 1896)[1] and by the aid of the critical quantities the conditions for the liquefaction of the examined gas may be found by starting from another gas with the same number of atoms in the molecule, which has been made liquid in a certain apparatus. By a corresponding process in an apparatus of the same form and of corresponding dimensions the examined gas may be made liquid.

The JOULE-KELVIN effect, which plays such an important part in the liquefaction of gases whose critical temperature lies below the lowest temperature down to which we can permanently cool down by the aid of evaporating liquefied gases, may be calculated from the isotherms, at least if the specific heat in the gas state is not unknown, and its determination, though more lengthy than that of the isotherms, may be an important test of our measurements. If there is to be question of statical liquefaction of the gas by means of the JOULE-KELVIN effect, this must at all events give a decrease of temperature at the lowest temperature already reached, which, as was demonstrated in the above communication, will be the case to a corresponding amount for gases with the same number of atoms[1]) in the molecule at corresponding states, while a monatomic gas compared with a di-atomic one will be in more favourable circumstances for liquefaction (comp. also Comm. N$^0$. 66, 1900).

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[1] Developed in view of the statical liquefaction of hydrogen and the obtaining of a permanent bath of liquid hydrogen (Comm. N$^0$. 94*f*) at which I was working then.

But the sign of the JOULE-KELVIN effect under certain circumstances does not decide the question whether an experiment on the statical liquefaction of a gas will succeed. Speaking *theoretically*, when by the JOULE-KELVIN effect at a certain temperature a decrease of temperature however slight can be effected, liquid may be obtained by an adiabatic process with a regenerator coil and expansion cock with preliminary cooling down of the gas to that temperature. But as long as we remain too near the point of inversion the JOULE-KELVIN effect will have a slight value; accordingly the processes by which really gas was liquefied in a statical state with an apparatus of this kind, as those which were applied to air by LINDE and HAMPSON, and to hydrogen by DEWAR, start from a much lower reduced temperature, viz. from about half the reduced temperature at which the sign of the JOULE-KELVIN effect at small densities is reversed, or more accurately from somewhat below the BOYLE-point, i. e. that temperature at which the minimum of $pv$ is found at very small densities. Experiments from which could be derived at how much higher reduced temperature the process still succeeds with monatomic gases are lacking. So according to the above theorem it is *practically* the question whether the lowest temperature at our disposal lies below this BOYLE-point[2]) which is to be calculated from the isotherms, in order that the JOULE-KELVIN effect may have a sufficient value to yield an appreciable quantity of liquid in a given apparatus in a definite time.

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[1]) The inversion points of the effect having reference to the amount 0 and therefore being independent of the number of atoms in the molecule, are at corresponding states, and the inversion point for small densities is at corresponding temperature for *all* gases as far as they obey the law of corresponding states. This is easily deduced from the considerations of Comm. N$^0$. 23.

[2]) The BOYLE-point, as well as the JOULE-KELVIN-inversion-point for small densities is a corresponding temperature and both are therefore theoretically proportional. In the present question it is better to refer to the BOYLE-point than to the JOULE-KELVIN-inversion-point, as between these two points association or any other deviation of the law of corresponding states occurring at lower temperatures can begin.

Three years ago I had so far advanced with the investigations which led to the isotherms of helium [1]), that these determinations themselves could be taken up with a reasonable chance of success.

At first the great difficulty was how to obtain sufficient quantities of this gas. Fortunately the Office of Commercial Intelligence at Amsterdam under the direction of my brother, Mr. O. KAMERLINGH ONNES, to whom I here express my thanks, succeeded in finding in the monazite sand the most suitable commercial article as material for the preparation, and in affording me an opportunity to procure large quantities on favourable terms. The monazite sand being inexpensive, the preparation of pure helium in large quantities became chiefly a matter of perseverance and care [2]).

The determination of isotherms of helium was not accomplished before 1907.

The results of the determinations of the isotherms were very surprising. They rendered it very probable that the JOULE-KELVIN effect might not only give a decided cooling at the melting point of hydrogen, but that this would even be considerable enough to make a LINDE-HAMPSON process succeed.

Before the determinations of the isotherms had been performed I had held a perfectly different opinion in consequence of the failure of OLSZEWSKI's and DEWAR's attempts to make helium liquid, and had even seriously considered the possibility that the critical temperature of helium might lie, if not at the absolute zero-point, yet exceedingly low. In order to obtain also in this case the lower temperatures, which among others are necessary for continuing the determinations of isotherms below the temperatures obtainable with solid hydrogen, I had e.g. been engaged in designing a helium motor (cf. Comm. N$^0$. 23) in which a vacuum glass was to move to and fro as a piston in another as a cylinder. And when compressed helium was observed to sink in liquid hydrogen (Comm. N$^0$. 96, Nov. 1906) I have again easily suffered myself to be led astray to the erroneous supposition of a very low critical temperature.

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[1]) Comp. for cryostats: Comm. N$^0$. 14, 51, 83, 94; for thermometry: Comm. N$^0$. 27, 60, 77, 93, 95, 99, 101, 102; for manometers, piezometers and determination of isotherms: Comm. N$^0$. 44, 50, 69, 70, 71, 78, 97, 99, 100.

[2]) Even the quantity of 200 liters (and 160 liters of reserve) of the extreme purity required, though asking a great deal of labour was not out of reach.

In the meantime I had remained convinced that only the determination of the isotherms could decide how helium could be made liquid. Hence we had proceeded with what might conduce to making a favourable result for the critical temperature at once serviceable. Thus the preparation of a regenerator coil with expansion cock in vacuum glass (to be used at all events below the point of inversion), and the preparation of pure helium was continued. Of the latter a quantity had even been gradually collected sufficiently large to render possible a determination of the JOULE-KELVIN effect in an apparatus already put to the test in prelimininary investigations, and to enable us to make efficient expansion experiments.

All at once all these preparations proved of the greatest importance when last year (Comm. N$^0$. 102*a*) the isotherms began to indicate 5° K. to 6° K. for the critical temperature, an amount which according to later calculations, which will be treated in a subsequent paper, might have been put slightly higher (e. g. 0.5°), and which was in harmony with the considerable increase of the absorption of helium by charcoal at hydrogen temperatures, on the strength of which DEWAR had estimated the critical temperature of helium at 8° K. For according to the above theorem it was no longer to be considered as impossible to make helium liquid by means of a regenerator coil, though this was at variance with the last experiments of OLSZEWSKI, who put the boiling point below 2° ¹).

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¹) If there is not accepted an improbably high value for the critical pressure of helium, than this comes practically to the same as if the critical point was estimated at below 2°, because the difference between the boiling point and the critical point cannot exceed some tenths of a degree. — Prof. OLSZEWSKI kindly drew my attention to the fact that in the original quotation of his statement in the present paper as well as in a previous one I erroneously had written critical point in stead of boiling point and I avail myself of this occasion to rectify my error. I remark that in the case of helium it was not to be considered as impossible that the critical pressure was below 1 Atm. (comp. § 4). But in this case experiments in which the gas is expanded from a high pressure to the

It is true that the conclusions drawn from the isotherms left room for doubt. It seemed to me that the isotherms at the lowest temperature yielded a lower critical temperature than followed from the isotherms at the higher temperatures, which is due to peculiarities, which have been afterwards confirmed by the determination of new points on the isotherms. So there was ample room for fear that helium should deviate from the law of the corresponding states, and that still lower isotherms than those already determined should give a still lower critical temperature than 5° K., and according as the critical temperature passed on to lower temperatures the chance to make helium liquid by means of the JOULE-KELVIN effect at the lowest temperatures to be reached with liquid hydrogen (solid hydrogen brings new complications with it) became less. This fear could not be removed by the expansion experiment which I made some months ago, and in which I had thought I perceived a slight liquid mist (Comm. N⁰. 105 Postscriptum March 1908). For in the first place only an investigation made expressly for the purpose could decide whether the mist was distinct enough, and whether the traces of hydrogen the presence of which could still be demonstrated spectroscopically, were slight enough to allow us to attach any importance to the phenomenon. And in the second place the mist was very faint indeed, which might point to a lower critical temperature than had been derived.

So it remained a very exciting question what the critical temperature of helium would be. And in every direction in which after the determination of the isotherms in hand we might try to get more information about it, we were confronted by great difficulties.

As, however, they consisted in the arrangement of a cycle with cooled helium, — a circulation being indispensable to integrate cooling effects with a reasonable quantity of helium [1]) — the labour spent for

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atmospheric pressure as were made by OLSZEWSKI cannot decide about the question if the gas can be liquefied or not at a certain temperature. The gas may become liquid at that temperature and yet have no *boiling point* at all, boiling becoming only possible at reduced pressure. It was therefore that in my expansion experiments I continued the expansion in vacuo.

[1]) Cf. p. 10 footnote 1.

years on the arrangement of the Leiden cascade of cycles for accurate measurements, might contribute to the surmounting of them. Arrived at this point I resolved to make the reaching of the end of the road at once my purpose, and to try to effect the statical liquefaction of helium with a circulation, as much as possible "corresponding" to my hydrogen circulation.

In this I perfectly realized the difficulty to satisfy at the same time the different conditions for success (allowing for possible deviations from the law of corresponding states). For though the reliability of the hydrogen cycle for the cooling down of the compressed helium to 15° K. was amply proved (Comm N$^0$. 103), the preliminary cooling to be reached was as to the temperature only just within the limit at which it could be efficient, nor were the other circumstances which could be realized, any more favourable.

Of course the scale on which the apparatus intended for the experiment in imitation of the apparatus which had proved effective for hydrogen, would be built, was not only chosen smaller in agreement with the value of $b$ which was put lower, but taken as small as possible. That the reduction of HAMPSON'S coil to smaller dimensions does not diminish its action had been found by former experiments, and has been very clearly proved by what OLSZEWSKI tells about the efficiency of his small hydrogen apparatus. I could not, however, reduce below a certain limit without meeting with construction problems, about which the hydrogen apparatus had not given any information. We had to be sure that the capillaries would not get stopped up, that the cocks would work perfectly, that the conduction of heat, viscosity etc. would not become troublesome. When in connection with the available material, the smallest scale at which I thought the apparatus still sufficiently trustworthy, reduction to half its size, had been fixed, the dimensions of the regenerator coil, though as small as those of OLSZEWSKI'S coil, proved still so large that the utmost was demanded of the dimensions of the necessary vacuum glasses; which was of the more importance, because the bursting of the vacuum glasses during the experiment would not only be a most unpleasant incident, but might at the same time annihilate the work of many months.

Besides the difficulties given by the helium liquefactor itself, the further arrangement of the cycle in which it was to be inserted, offered many more.

The gas was to be placed under high pressure by the compressor, and was to be circulated with great rapidity. Every contamination was to be avoided, and the spaces which were to be filled with gas under high pressure were to have such a small capacity, that they only held part of the available naturally restricted quantity of helium.

As compressor only CAILLETET's modified compressor could be used, a compressor with mercury piston, which in conjunction with an auxiliary compressor had been arranged for experiments with pure and costly gases, and was described in Comm. N$^0$. 14 (Dec. 1894) and Comm. N$^0$. 54 (Jan. 1900), and which also served for the compression of the helium in the expansion experiments of last March (Comm. No. 105)[1]).

That it could only be charged to 100 atms., a fact which I had sometimes considered as a drawback in the case of experiments with helium, could no longer be deemed a drawback after the determinations of isotherms had taught that even if the pressure of helium compressed above 100 atms. at low temperatures is raised much, the density of the gas increases but little. Accordingly I have not gone beyond 100 atms. in my expansion experiments. The higher pressures which DEWAR and OLSZEWSKI applied in their expansion experiments, have been a decided disadvantage, because they involved the use of a narrower expansion tube. With regard to the circulation now to be arranged, with estimation of the critical pressure at 7 or 5 atms.[2]), according as $b$ was put at a third or half that of hydrogen, a pressure of 100 atms. in the regenerator coil had to be considered as sufficient according to the law of corresponding states.

---

[1]) Just as when it was used to get a permanent bath of liquid oxygen (completed 1894, Comm. N$^0$. 14) it was now again in the pioneering cycle and rewarded well the work spent on it especially in 1888 when I was working at the problem to pour off liquid oxygen in a vessel under atmospheric pressure by the help of the ethylene cycle.

[2]) The results of the isotherm of helium at — 259° to be treated in a following communication were not yet available then; they point to a smaller value.

But for a long time it was considered an insuperable difficulty that the compressor conjugated to the auxiliary compressor could circulate at the utmost 1400 liters of gas measured at the ordinary temperature per hour, $^1/_{15}$ of the displacement with the hydrogen circulation. Not before experiments with the latter had been made, in which the preliminary cooling of the hydrogen did not take place with air evaporating at the vacuumpump (so at — 205°) but under ordinary pressure (so at — 190°), and moreover the hydrogen compressor ran 4 times more slowly than usual, and in these experiments liquid hydrogen had yet been obtained, it might be assumed that the circulation process to be realized would still be sufficient to accumulate liquid helium.

With regard to the parts of the compressors, the auxiliary apparatus, and the conduits, which in the course of the experiment assume the same pressure as the regenerator coil, their joint capacity was small enough to enable us to make the experiment with a quantity of 200 liters. This quantity of pure helium besides a certain quantity (160 liters) kept in reserve could be ready within not too long a time [1]).

A great difficulty of an entirely different nature than the preceding one consisted in this that the hydrogen circulation and the helium circulation could not be worked simultaneously with the available helpers to work them. It is true that the two circulations have been arranged not only for continuous use, but if there is a sufficient number of helpers, also for simultaneous use, but in a first experiment it was out of the question to look, besides after the helium circulation, also after the hydrogen circulation, the working of which requires, of course, great experience [2]). So on the same day that the helium experiment was to be made, a store of liquid hydrogen had to be previously prepared large enough to provide for the required cooling during the course of the helium experiment. It was again the law of corresponding states which directed us in the estimation of the duration of the experiment and the required quantity of liquid hydrogen [1]. They remained just below the limit at which the arrangement of the experiment in the designed way would be unadvisable, but how near this limit was has appeared later.

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[1]) Success was only possible by applying the cycle method; this is evident from the fact that the helium has passed the valve 20 times before liquefaction was observed, and the considerable labour that would have been to expend on the preparation of 20 times the quantity of the pure helium used would have been increased in the same proportion i. e. to an extravagant amount.

[2]) Now the great difficulties of a first liquefaction have been overcome simultaneous working has become possible, though it remains the question how to find the means to develop the laboratory service according to the extension of its field of research.

In all these considerations the question remained whether everything that could appear during the experiment, had been sufficiently taken into account in the preparation. So we were very glad when the calculation of the last determined points on the isotherm of — 259° shortly before the experiment confirmed that the BOYLE-*point* though below the boiling point of hydrogen lay somewhat above the lowest temperature of preliminary cooling, and at least the foundation of the experiment was correct.

In the execution I have availed myself of different means which DEWAR has taught us to use. I have set forth the great importance of his work in the region of low temperatures in general elsewhere (Comm. Suppl. N$^0$. 9, Febr. 1904), here, however, I gladly avail myself of the opportunity of pointing out that his ingenious discoveries, the use of silvered vacuum glasses, the liquefaction of hydrogen, the absorption of gases in charcoal at low temperatures, together with the theory of VAN DER WAALS, have had an important share in the liquefaction of helium.

§ 2. *Description of the apparatus.* The whole of the arrangement has been represented on Pl. I. We mentioned before that in virtue of the principles set forth in Comm. N$^0$ 23 the construction of the helium liquefactor (see Pl. II and III) was as much as possible an imitation of the model of the hydrogen liquefactor described before (Comm. N⁰. 94*f*, May 1906), to which I therefore refer in the first place.

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[1] The hydrogen cycle is not only arranged so that the same pure hydrogen in it can be circulated and liquefied at the rate of 4 liters per hour as long as this is wished, but also allows (as will be treated in a following communication) easily to prepare great stores of extremely pure hydrogen gas, which can be tapped off from the apparatus as liquid at the rate of 4 liters per hour.

It was particularly difficult to keep the hydrogen, which evaporating under a pressure of 6 cm. is to cool the compressed helium to 15° K. (just above the melting point of hydrogen), on the right level in the refrigerator intended for this purpose. This difficulty was surmounted in the following way. The liquid hydrogen is not immediately conveyed from the store bottles into the refrigerator, but first into a graduated glass *Ga* in the way indicated before, which when comparing the figures of Comm. N⁰. 94*f* and N⁰. 103 Pl. I fig. 4 does not require a further explanation. This graduated glass was a not-silvered vacuum glass, standing in a silvered vacuum glass *Gb* with liquid air, in which on either side the silver coating had been removed over a vertical strip so as to enable us to watch the level of the hydrogen in the graduated glass. From this vacuum glass the liquid hydrogen is siphoned over into the hydrogen refrigerator by means of a regulating cock *P*. To see whether the level of the liquid in the refrigerator takes up the right position, the german-silver reservoir $N_1$ of a helium thermometer has been soldered to the tube which conveys at an initial temperature of — 190° the compressed helium which is to be cooled down further. This reservoir leads trough a steel capillary $N_2$ (as in Comm. N⁰. 27, May 1896) to a reservoir $N_4$ with stem $N_3$. The quantity of helium and the pressure have been regulated in such a way that the mercury stands in the top of the stem, when the thermometer reservoir is quite immerged in hydrogen of 15° K., while as soon as the level falls, this is immediately shown by the fall of the mercury. The same purpose is further served by two thermo-elements constantan-iron (see Comm. N⁰. 89, Nov. 1903 and N⁰. 95*a*, June 1906), one on the bottom, the other soldered to the spiral on the same level as the thermometer reservoir. They did not indicate the level in the experiment of July 10th, because something got defect.

The evaporated hydrogen contributes in the regenerator *Db* to save liquid air during the cooling of the compressed helium, and is sucked up (along 15 and *Hc*) in the large cylinder of the conjugated methylchloride pump (Comm. N⁰. 14, Dec. 1894), which otherwise serves in the methylchloride circulation of the cascade for liquid air; it is further conducted through an oil-trap, and over charcoal to the hydrogen gas-holder (Comm. N⁰. 94*f*), from which the hydrogen compressor (Comm. N⁰. 94*f*) forces the gas again into the store cylinders.

To fill the helium circulation the pure helium passes from the cylinders $R_1$ (see Pl. II), in which it is kept, into the gasholder floating on oil (cf. Comm. N⁰. 94*f*), which is in connection with the space in which the helium expands when issuing from the cock, a german-silver cylinder, in which the upper part of the vacuum glass *Ea* has been inserted. The gas from the gasholder, and afterwards the cold outflowing helium, which has flowed round the regenerator coil, and of whose low temperature we have availed ourselves in the regenerator *Da* to save liquid air when cooling the compressed helium, is sucked up by the auxiliary compressor *V*, and then received in the compressor with mercury piston *Q* (comp. Comm. N⁰. 54). This forces it (Pl. II and III) along the conduit:

*a*. through a tube *Ca* which at its lower end is cooled down far below the freezing point by means of vapour of liquid air, and at its upper end is kept at the ordinary temperature. Here the helium is perfectly dried.

*b*. through a tube divided into two parts along two refrigerating tubes (in *Da* and *Db*), in which it is cooled in the one by the abduced hydrogen, in the other by the abduced helium, after which it unites again.

*c*. through a tube *Cb* filled with exhausted charcoal and immerged in liquid air. Here whatever traces of air might have been absorbed during the circulation, remain behind.

*d*. through a refrigerating tube $B_3$ lying in the liquid air which keeps the cover of the hydrogen space and of the helium space cooled down.

*e*. through a refrigerating tube $B_2$, in which it is cooled by the evaporated liquid hydrogen.

*f*. through the refrigerating tube $B_1$ lying in the liquid hydrogen evaporating under a pressure of 6 cm., here the compressed helium is cooled down to 15° K.;

*g*. and from here in the regenerator coil *A*, which has been fourfold wound as in HAMPSON's apparatus for air, and in the hydrogen liquefactor of Comm. N⁰. 94*f*.

Then it expands through the cock $M_1$. If it should allow too much gas to pass, this can escape through a safety tube. When the temperature has descended so low that the liquid helium flows out, the latter collects in the lower part of the vacuum glass *Ea*, which is transparent up to the level of the cock, and is silvered above it.

The outflowing gaseous helium can be made to circulate again by the compressor of the circulation, or be pressed in the supply cylinder $R_2$.

At some distance under the expansion cock $M_1$, the german silver reservoir $Th_1$ of a helium thermometer has been adjusted, it is soldered to a steel capillary $Th_2$, which is connected with the manometer reservoir $Th_4$ with stem $Th_3$. If the mercury has been adjusted in such a way that at 15° K. its level is at the lower end of the just mentioned stem, the stem has sufficient length to prevent the mercury from overflowing into the capillary with further fall of the temperature.

The circulation is provided with numerous arrangements for different operations (for the compressor comp. Comm. N⁰. 54). Worth mentioning is an auxiliary tube *Z* filled with exhausted charcoal, which is cooled by liquid air when used. After the whole apparatus has been filled with pure gas, the gas is circulated through this side-conduit (along 11 and 8) while the charcoal tube *Cb* belonging to the liquefactor is shut off (by *M* and 9), to free it from the last traces of air which might have remained in the compressor and the conduits.

It now remains to describe in what way it has been arranged that the liquid helium can be observed. Round the transparent bottom part of the vacuum glass a protection of liquid hydrogen has been applied. The second vacuum glass *Eb*, which serves this purpose, forms a closed space together with the former *Ea*, and the construction has been arranged in such a way that first this space can be exhausted and filled with pure hydrogen gas, which is necessary to keep the liquid hydrogen perfectly clear later on. The liquid hydrogen is again conducted into this space in the way of Comm. N⁰. 94*f* and N⁰. 103 Pl. I fig. 4; the evaporated hydrogen escapes at *Hg* to the hydrogen gasholder. The hydrogen glass is surrounded by a vacuum glass *Ec* with liquid air, which in its turn is surrounded by a glass *Ed* with alcohol, heated by circulation.

By these contrivances and the extreme purity of the helium we succeeded in keeping the apparatus perfectly transparent to the end of the experiment, after 5 hours. Protection with liquid hydrogen is necessary to reduce the evaporation of the helium to an insignificant degree notwithstanding that the silver coatings of the vacuum glass have been removed. That it ended in a narrower part, and the helium thermometer reservoir was not placed at the lowest point, was because it was possible that only an exceedingly slight amount of liquid should be formed. The vacuum glass was made transparent up to the cock in order to enable us to see any mist that might appear and if on the other hand much liquid was formed, to prevent the lower part from getting entirely filled without our noticing it. The latter has actually been the case for some time, and would not have been so soon perceived, if the walls had been silvered further. But if the glass is not silvered, the transport of heat towards the helium is much greater, and without protection with liquid hydrogen the helium that was formed might have immediately evaporated.

In the preparation of the vacuum glasses [1] Mr. O. KESSELRING, glassblower of the laboratory, has met the high demands put to him, with untired zeal and devotion, for which I here gladly express my thanks to him.

§ 3. *The helium.* As to the chemical part of the preparation of this gas I was successively assisted by Mr. J. WATERMAN, Mr. J. G. JURLING, Mr. W. MEYER-CLUWEN, and Mr. H. FILIPPO Jzn. Chem. Docts., who collaborated with Mr. G. J. FLIM, chief of the technical department of the cryogenic laboratory. To all of them I gladly express my indebtedness for the share each of them has had in the arrangement, the improvement, and the simplification of the operation. More particularly to Mr. FILIPPO for his carefull analyses and the way, in which the last combustion over CuO with addition of oxygen, and avoidance of renewed contamination by hydrogen was carried out by him.

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[1] There was one of each in reserve before the beginning of the experiment. Only one of these reserve glasses had to be used.

The gas was obtained from the monazite (see § 1) by means of heating, it was exploded with oxygen. Then it was burned over CuO and the oxygen and gases of the same volatility were removed by freezing them out in liquid hydrogen. Then it was compressed over charcoal at the temperature of liquid air, after which it was under pressure led over charcoal at the temperature of liquid hydrogen several times till the gas which had been absorbed in the charcoal and then separately collected no longer contained any appreciable admixtures.

This way of preparation (to be treated in a following Comm.) was also applied in Comm. N⁰. 105.

§ 4. *The experiment.* After on July 9th the available quantity of liquid air had been increased [1]) to 75 liters, all apparatus examined as to their closures, exhausted, and filled with pure gas, we began the preparation of liquid hydrogen on the 10th of July, 5.45 a. m., 20 liters of which was ready for use in silvered vacuum glasses (cf. Comm. N⁰. 94*f*) at 1.30 p. m. In the meantime the helium apparatus had been exhausted while the tube with charcoal belonging to it was heated, and this tube being shut off, the gas contained in the rest of the helium circulation was freed from the last traces of air by conduction over charcoal in liquid air trough the sideconduit. The hydrogen circulation of the helium apparatus was connected with the hydrogen gasholder and the air-pump, which had served as methyl-chloride pump in the preparation of liquid air the day before, and this whole circulation was exhausted for so far as this had not been done before, and filled with pure hydrogen. Moreover the space between the vacuum glasses (*Ea* and *Eb*) which was to be filled with liquid hydrogen as a protection against access of heat, was exhausted and filled with pure hydrogen, and the thermometers and thermoelements were adjusted.

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[1]) With the help of the regenerative cascade (cf. Comm. N⁰. 94*f* XIII and Suppl. N⁰ 18*a*).

At 1.30 p. m. the cooling and filling of the glasses which, filled with liquid air, were to protect the glasses which were to be filled with liquid hydrogen, began with such precautions that everything remained clear when they were put in their places. At 2.30 a commencement was made with the cooling of the graduated vacuum glass and of the hydrogen refrigerator of the helium liquefactor by the aid of hydrogen led trough a refrigerating tube, which was immerged in liquid air. At 3 o'clock the temperature of the refrigerator had fallen to — 180° according to one of the thermo-elements. Then the protecting glass (*Eb*) was filled with liquid hydrogen, and after some delay in consequence of insignificant disturbances, the filling of the graduated vacuum glass and the hydrogen refrigerator with hydrogen began at 4.20 p. m.

At the same time the helium was conducted in circulation through the liquefactor. The pressure under which the hydrogen evaporated, was gradually decreased to 6 cm., at which it remained from 5.20 p. m. The level in the refrigerator was continually regulated aocording to the indication of the thermometer-level-indicator and the reading of the graduated glass, and care was taken to add liquid hydrogen (*Hydr. a*, *Hydr. b* Pl. II) and liquid air wherever necessary (*a*, *b*, *c*, *d*, Pl. II). In the meantime the pressure of the helium in the coil was slowly increased, and gradually raised from 80 to 100 atms. between 5.35 and 6.35 p. m.

At first the fall of the helium thermometer which indicated the temperature under the expansion cock, was so insignificant, that we feared that it had got defect, which would have a been double disappointment because just before also in the gold-silver thermo-element, which served to indicate the same temperature, some irregularity had occurred. After a long time, however, the at first insignificant fall began to be appreciable, and then to accelerate. Not before at 6.35 an accelerated expansion was applied, on which the pressure in the coil decreased from 95 to 40 atms., the temperature of the thermometer fell below that of the hydrogen. In successive accelerated expansions, especially when the pressure was not too high, a distinct fluctuation of the temperature towards lower values was clearly observed. Thus the thermometer indicated e. g. once roughly 6° K.

In the meantime the last bottle of the store of liquid hydrogen was connected with the apparatus: and still nothing had as yet been observed but some slight waving distortions of images near the cock. The thermometer indicated first even an increase of temperature with accelerated expansion from 100 atms., which was an indication for us to lower the circulation pressure to 75 atms. Nothing was observed in the helium space then either, but the thermometer began to be remarkably constant from this moment with an indication of less than 5° K. When once more accelerated expansion from 100 atms was tried, the temperature first rose, and returned then to the same constant point.

It was, as Prof. SCHREINEMAKERS, who was present at this part of the experiment, observed, as if the thermometer was placed in a liquid. This proved really to be the case. In the construction of the apparatus (see § 2) it had been foreseen that it might fill with liquid, without our observing the increase of the liquid. And the first time the appearance of the liquid had really escaped our observation. Perhaps the observation of the liquid surface which is difficult for the first time under any circumstance, had become the more difficult as it had hidden at the thermometer reservoir. However this may be, later on we clearly saw the liquid level get hollow by the blowing of the gas from the valve and rise in consequence of influx of liquid on applying accelerated expansion, which even continued when the pressure descended to 8 atms. So there was no doubt left that the critical pressure lies also above one atmosphere. If it had been below it, the apparatus might all at once have been entirely filled with liquid compressed above the critical pressure, [which by heating would have passed continously into the gaseous state,] and only with decrease of pressure a meniscus would have appeared somewhere in the liquid layer; this has not taken place now.

The surface of the liquid was soon made clearly visible by reflection of light from below, and that unmistakably because it was clearly pierced by the two wires of the thermoelement.

This was at 7.30 p. m. After the surface had once been seen, it was no more lost sight of. It stood out sharply defined like the edge of a knife against the glass wall. Prof. KUENEN, who arrived at this moment, was at once struck with the fact that the liquid looked as if it was almost at its critical temperature. The peculiar appearance of the helium may really be best compared with that of a meniscus of carbonic acid e.g. in a CAGNIARD DE LA TOUR-tube. Here, however, the tube was 5 cm. wide. The three liquid levels in the vacuum glasses being visible at the same time, they could easily be compared; the difference of the hydrogen and the helium was very striking.

When the surface of the liquid had fallen so far that 60 cm$^3$. of liquid helium still remained — so considerably more had been drawn off — the gas in the gasholder was exhausted, and then the gas which was formed from this quantity of liquid was again separately collected. In the course of the experiment the purity of this gas was determined by means of a determination of the density (2.01), which was afterwards confirmed by an explosion experiment with oxyhydrogen gas added, and further by a careful spectroscopical investigation.

At 8.30 the liquid was evaporated to about 10 cm$^3$., after which we investigated whether the helium became solid when it evaporated under decreased pressure. This was not the case, not even when the pressure was decreased to 2.3 cm. A sufficient connection could not be quickly enough etablished with the large vacuumpump, which exhausts to 2 mm., so this will have to be investigated on another occasion. The deficient connection, however, has certainly made the pressure decrease below 1 cm., and perhaps even lower. That 7 mm. has been reached, is not unlikely.

At 9.40 only a few cm$^3$. of liquid helium were left. Then the work was stopped. Not only had the apparatus been strained to the uttermost during this experiment and its preparation, but the utmost had also been demanded from my assistants.

But for their perseverance and their ardent devotion every item of the program would never have been attended to with such perfect accuracy as was necessary to render this attack on helium successful.

In particular I wish to express my great indebtedness to Mr. G. J. FLIM, who not only assisted me as chief of the technical department of the cryogenic laboratory in leading the operations, but has also superintended the construction of the apparatus according to my direction, and rendered me the most intelligent help in both respects.

§ 5. *Control experiments.* All the gas that had been used in the experiment, was collected in three separate quantities and compressed in cylinders. Quantity $A$ contains what was finally left in the apparatus. Quantity $B$ has been formed by evaporation of a certain quantity of liquid helium. Quantity $C$ is the remaining part that has been in circulation. Together they yielded the same quantity as we started with. They were all three exploded with addition of oxyhydrogen gas and excess of oxygen; no hydrogen could be demonstrated. For the density (in a single determination) we found $(O = 16)$ $A = 2.04$, $B = 1.99$, $C = 2.02$.

The spectrum of the gas used for the experiment put in a tube with mercury closure without electrodes and freed beforehand from vapour of water and fat at the temperature of liquid air, answered (only the spectrum of the capillary has been investigated) the description given by COLLIE of the spectrum of helium with a trace of hydrogen and mercury vapour.

Spectroscopically both the distilled $C$, and $B$ were somewhat purer than the original gas. In the latter the hydrogen lines gained in case of high vacua, in the former the helium disappeared last. The hydrogen, from which the latter has still been cleared, must be found in $A$. By means of absorption by charcoal 8 cm$^3$. of hydrogen was separated from this. To this would correspond a difference in percentage of hydrogen before and after the experiment of 0.004 $^0/_0$.

To estimate the percentages of hydrogen the spectra of the justmentioned quantities were compared with the spectrum of a helium which could not contain much more than 0.005 $^0/_0$ hydrogen according to an estimation founded on the quantites of hydrogen which had been absorbed from the gas the last few times of successive purification when it was led compressed over charcoal at the temperature of liquid hydrogen, and with the spectrum of this helium after 0.1 $^0/_0$ hydrogen had been mixed with it.

The gas used for the experiment did not differ much from that which served for comparison, and of which the red hydrogen and helium lines vanished simultaneously for the highest vacua, but it seemed to be somewhat less pure, for the red hydrogen line preponderated over the helium line for the highest vacua. In the different spectra the hydrogen line $C$ was not to be seen at a pressure of 32 mm., the $F$-line with an intensity of 0.01 of He 5016; at 12—16 mm. $C$ was faint compared with He 6677, and $F$ faint compared with He 5016. An amount varying between 0.01 and 0.3 was estimated for the ratio of the intensity.

On the other hand at 32 mm. the $C$ in the mixture with 0.1 pCt. hydrogen had already the same intensity as He 6677, $F$ 0.3 of He 5016, which remained the case at 16 mm. (somewhat less for $C$, somewhat more for $F$).

In spite of the precautions taken it was observed a single time that the hydrogen lines increased in intensity during the determination, so when we proceeded to lower pressures the determinations became unreliable. These comparisons are, therefore, very imperfect; but then, the examination how traces of hydrogen in helium may be quantitatively determined by a spectroscopic method would constitute a separate investigation. In connection with the above difference in content of $B$ and $C$ with the original gas, the observations mentioned may perhaps serve to show that these percentages have not been much more than 0.004 and 0.008.

The purity of the helium had already been beyond doubt before, for the cock worked without the least disturbance, and no turbidity was observed even in the last remaining 2 $cm^3$. of liquid.

The reliability of the helium thermometer was tested by the determination of the boiling point of oxygen, for which 89° K. was found instead of 90° K. We must, however, bear in mind that the thermometer has not been arranged for this temperature and the accuracy in percents of the total value is considerably higher for the much lower temperature of liquid helium.

For the assistance rendered me in the different control experiments, I gladly express my thanks to Dr. W. H. KEESOM and Mr. H. FILIPPO Jzn.

§ 6. *Properties of the helium.* By the side of important points of difference the properties of helium present striking points of resemblance with the image which DEWAR drew in his presidential address in 1902 on the strength of different suppositions.

We mentioned already the exceedingly slight capillarity.

For the boiling-point we found 4°.3 on the helium thermometer of constant volume at 1 atm. pressure at about 20° K. This temperature is still to be corrected to the absolute scale by the aid of the equation of state of helium. The correction may amount to some tenths of a degree if $a$ increases at lower temperatures, so that the boiling-point may perhaps be rounded off to 4°.5 K.

The triple-point pressure if it exists lies undoubtedly below 1 cm., perhaps also below 7 mm. According to the law of corresponding states the temperature can be estimated at about 3° K. at this pressure. The viscosity of the liquid is still very slight at this temperature. If the helium should behave like pentane, we could descend to below 1.5° K. before it became viscous, and still lower near 1° K. before it became solid. How large the region of low temperatures (and high vacua) is that has now been opened, is, however, still to be investigated.

Liquid helium has a very slight density, viz. 0.15. This is smaller than was assumed and gives also a considerably higher value of $b$ than can be derived from the isotherms at — 252°.72 and — 258°.82 now that the points mentioned in § 1 have been determined, viz. about 0.0007 provisionally. The value of $b$ which follows from the liquid state is about double the value of $b$ which was expected (viz. 0.0005), and which was assumed in the calculations of Dr. KEESOM and myself on mixtures of helium and hydrogen, cf. Suppl. N°. 16, Sept. '07, p. 4 footnote 4.

From the high value of $b$ follows immediately a small value of the critical pressure, which probably lies in the neighbourhood of 2 or 3 atms., and is exceedingly low in comparison with that for other substances. So when helium is subjected to the highest pressures possible, the "reduced" pressures become much higher than are to be realized for any other substance. What may be obtained in this respect by exerting a pressure of 5000 atms. on helium exceeds what would be reached when we could subject carbonic acid e.g. to a pressure of more than 100.000 atms.

The ratio of the density of the vapour and that of the liquid is about 1 to 11 at the boiling-point. It points to a critical temperature which is not much higher than 5° K., and a critical pressure which is not much higher than 2.3 atms.

But all the quantities mentioned will have to be subjected to further measurements and calculations before they will be firmly established, and before definite conclusions may be drawn from them.

We may only still mention here a preliminary value of $a$, viz. 0.00005 When in 1873 VAN DER WAALS in his Thesis for the Doctorate considered whether hydrogen would have an $a$, it was only after a long deliberation that he arrived at the conclusion that this must exist, even though it should be very small. It may be presumed that matter will always have attraction, was his argument, and as chance would have it, these words were repeated by him in reference to helium some days before the liquefaction of it (Proc. Kon Akad. Amsterdam June 1908). The $a$ found now denotes the smallest degree of this attraction of matter known to us (cf. Suppl. N⁰. 9, p. 13), which still manifests itself with remarkable clearness also in helium in its liquefaction.

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

## Supplement No. 15
## to No. 97—108.

**Dr. H. KAMERLINGH ONNES and Dr. W. H. KEESOM.** "Contributions to the knowledge of the $\psi$-surface of VAN DER WAALS. XV. The case that one component is a gas without cohesion with molecules that have extension. Limited miscibility of two gases." (*With two plates*).

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam,* **23 Febr**. p. 754—763, **30 Maart** p. 851—854 en **24 Mei 1907**, p. 59—66).

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**PLATE I.**

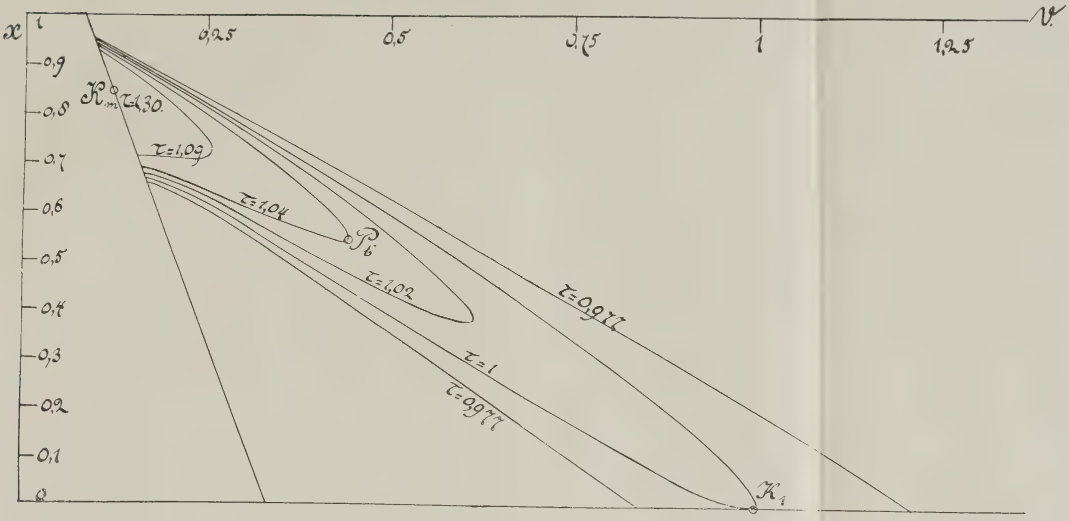


Fig. 1.

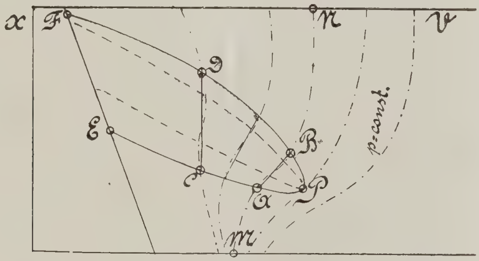
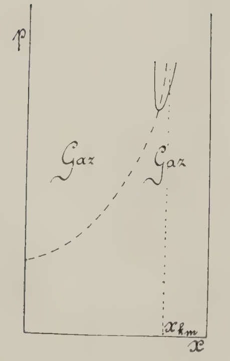


Fig. 2.



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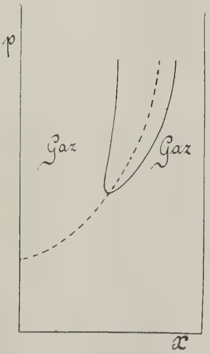


Fig. 2.

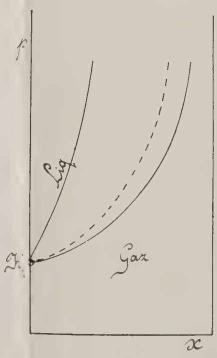
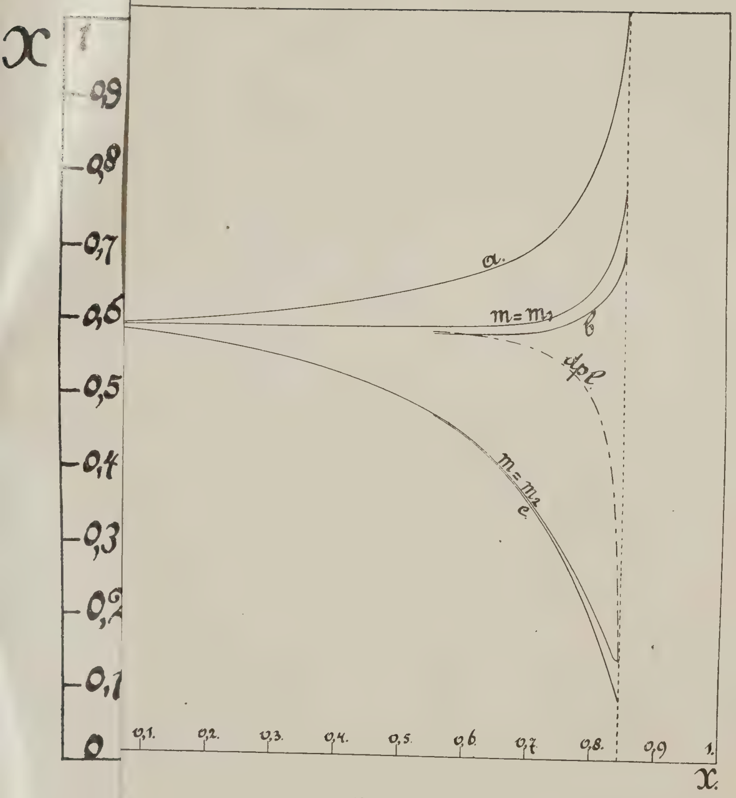


Fig. 3.

Communication Supplement No. 15.


x
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a.
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dpl.
m = m₂
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0,5.
0,6
0,7
0,8.
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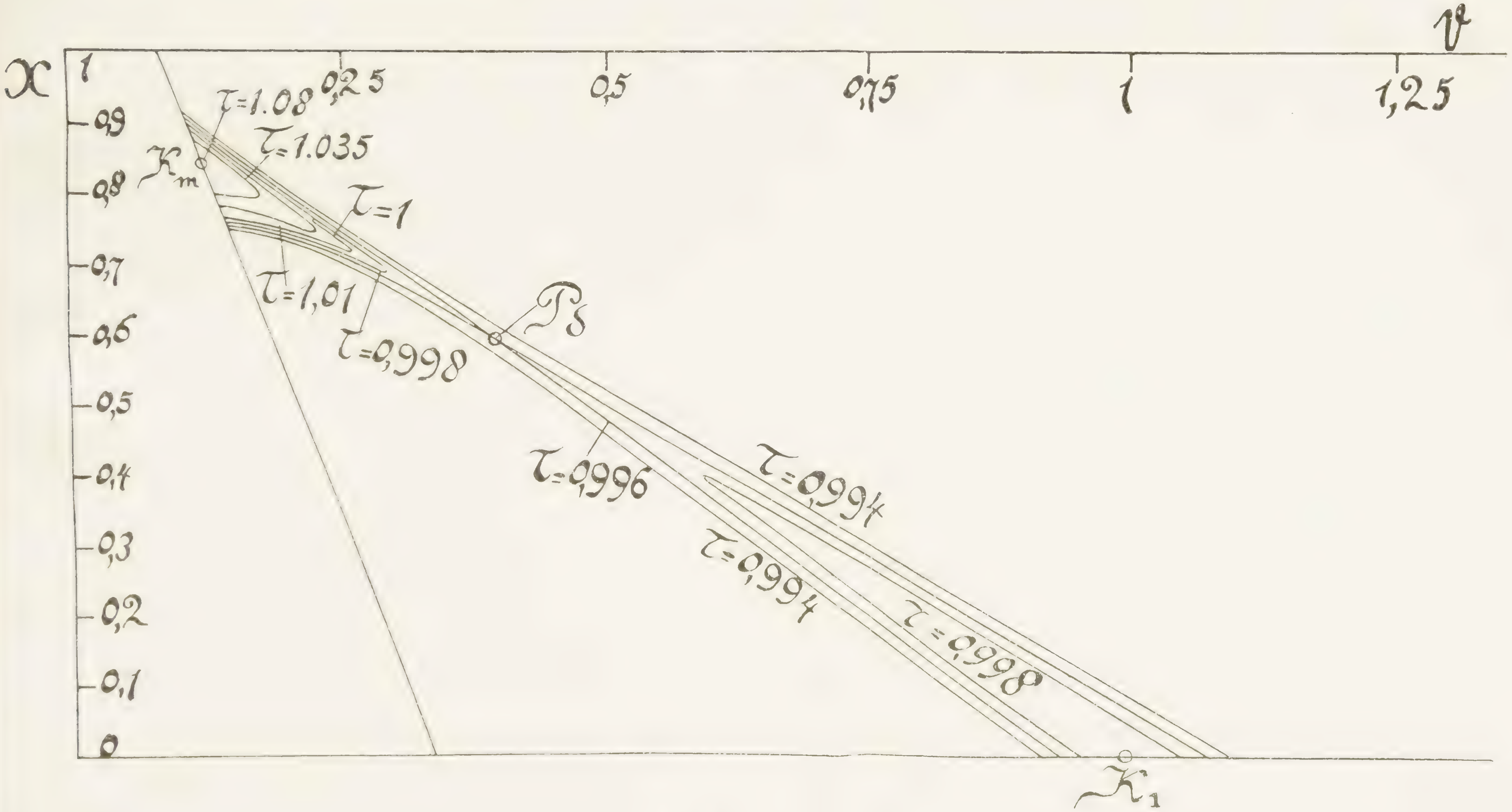
1.
x.

Fig. 2.

Dr. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. "Contributions to the knowledge of the $\psi$-surface of VAN DER WAALS. XV. The case that one component is a gas without cohesion with molecules that have extension. Limited miscibility of two gases."

PLATE II.



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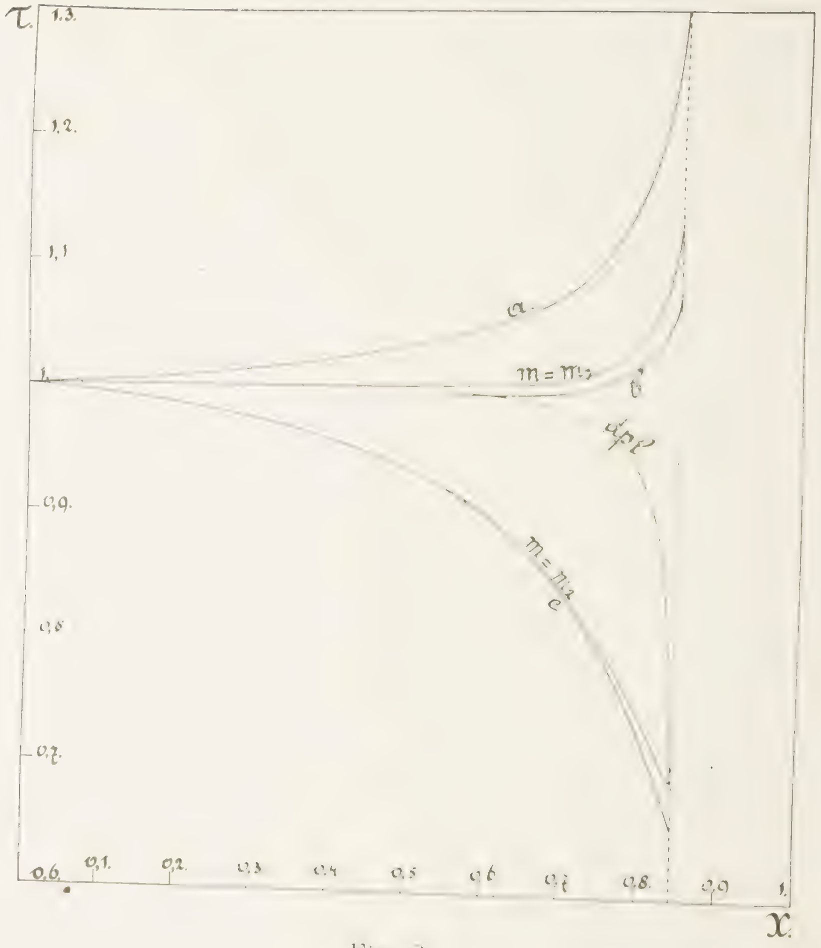

Fig. 2.

ommunication Supplement No 15.

**Dr. H. KAMERLINGH ONNES and Dr. W. H. KEESOM.** "*Contributions to the knowledge of the ψ-surface of* VAN DER WAALS. XV. *The case that one component is a gas without cohesion with molecules that have extension. Limited miscibility of two gases.*"

(February 23, 1907).

§ 1. *Introduction.*

In Comm. N⁰. 96*b* p. 10 it was mentioned that the investigation of the ψ-surface of binary mixtures in which the molecules of one component have extension but do not exert any attraction, would be taken in hand as a simpler case for a comparison with what the observations yield concerning mixtures of He, whose molecules are almost without cohesion. Before long we hope to give a fuller discussion of such a ψ-surface [1]). In the meantime some results have already been obtained in this investigation, which we shall give here.

Thus it has appeared, that at suitable temperatures, at least if the suppositions mentioned in § 2 concerning the applicability of VAN DER WAALS's equation of state with $a$ and $b$ not depending on $v$ and $T$ for constant $x$, hold for these mixtures [2]), *two different phases may be in equilibrium which must be both considered as gasphases.* Then the two substances which are the components of these mixtures, are *not miscible in all proportions even in the gas state.* And if certain conditions are fulfilled this may continue to be the case when the one component is not perfectly without cohesion, but possesses still some degree of cohesion, which, however, must be very slight.

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[1]). VAN LAAR, Proc. Kon. Akad. van Wet. Amst. May '05 p. 38, cf. p. 39 footnote 1, treated the projection of the plaitpoint curve on the $v$, $x$-plane for such a mixture, without, however, further investigating the shape of the spinodal curve and of the plait.

[2]) The possibility of the occurrence of a longitudinal plait at temperatures above the critical ones of both components was supposed by VAN DER WAALS in his treatment of the influence of the longitudinal plait on critical phenomena (Zittingsversl. Kon. Akad. v. Wet. Amst. Nov. 1894, p. 133). In his General Theory of the Plaits and the ψ-surface of VAN DER WAALS in the symmetrical case (Arch. Néerl. 24 (1891) p. 295) KORTEWEG had already drawn such a plait (Pl. XIII fig. $A_1$ l.c.)

From the considerations of VAN DER WAALS, Contin. II p. 41 sqq. and p. 104, follows that the mixing of two substances in the fluid state is brought about in consequence of the molecular motion depending on the temperature $T$, and promoted by the mutual attraction of the molecules of the two components determined by the quantity $a_{12}$, whereas the attractions of the molecules of each component inter se, determined by $a_{11}$ and $a_{22}$, oppose the mixing. If the mutual attraction of the molecules of the two components $a_{12}$ is small compared with the attraction of the molecules of one of the components inter se, $a_{11}$, the appearance of complete miscibility will be determined solely by the molecular motion, and then the temperature will have to be raised to an amount which, if some ratios of the $b$'s can occur then, may greatly exceed the critical temperature of the least volatile component, $T_{k_1}$ [1]), and with it the critical temperatures of all mixtures of these components. Thus from the equation ($a$) of VAN DER WAALS, Contin. II p. 43, follows $T_{km} = 1.6875\ T_{k_1}$ for the critical temperature of complete miscibility (VAN DER WAALS l. c.) $T_{km}$, if $a_{22} = a_{12} = 0$ and $b_{11} = b_{22}$ may be put. At a lower temperature the two substances considered are only partially miscible, whereas for such a temperature above $T_{k_1}$ there may be coexistence of two phases which, as will be further explained in §§ 3 and 4, are to be considered as gas phases.

Now it seems to follow from the nature of most of the substances known to us, most likely from the structure of their atoms, that $b_{22}$ is also small, when $a_{22}$ becomes very small; hence for a gas without cohesion $b_{22}$ may not be put equal to $b_{11}$ of a gas with cohesion, and as according to VAN DER WAALS's equation quoted above a small value of $b_{22}$ furthers the mixing greatly, the critical temperature of complete miscibility cannot rise as high as was derived just now. But though most likely the case mentioned just now as example does not occur in nature, yet it is certainly conducive to a better insight of what is to be expected for gases of exceedingly slight cohesion.

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[1]) VAN DER WAALS, in the paper cited p. 3 footnote 2, brought this in connection with the great amount of heat absorbed at the mixing of such substances

§ 2. *The shape of the spinodal curves and the form of the plait on the $\psi$-surface for binary mixtures of which one component is a gas with molecules with extension and without cohesion.* In fig. 1 Pl. I the spinodal curves are represented for such a case. The figure refers to the $\psi$-surface for the unit of weight of the mixtures, as we hope to give a further discussion of such a $\psi$-surface (comp. § 1), also with a view to the treatment of the barotropic phenomena which may occur for these mixtures [1]) in case of a suitable proportion of the molecular volumes of the components, for which treatment the use of the $\psi$-surface for the unit of weight readily suggests itself. As was also mentioned in Comm. N°. 96*b*, the conditions for coexistence may be studied by the aid of the $\psi$-surface for the unit of weight in the same way as by the aid of that for the molecular quantity; moreover it is easy to pass from the former to the latter, which offers advantages for the treatment of many problems (cf. § 6), if this is desired.

The equation of the spinodal curve on the $\psi$-surface for the unit of weight of mixtures, for which VAN DER WAALS's equation of state for binary mixtures with $a$ and $b$ not depending on $v$ and $T$ for constant $x$ may be applied, and for which $a_{12} = \sqrt{a_{11} a_{22}}$, $b_{12M} = {}^1\!/_2 \, (b_{11M} + b_{22M})$ (cf. Comm. No. 96*c*, p. 21) may be put [2]), runs:

$$R_1 R_2 T v^3 = 2 R_2 (1-x) \{ v\sqrt{a_{11}} - b_{11}\sqrt{a} \}^2 + \\ + 2 R_1 x \{ v\sqrt{a_{22}} - b_{22}\sqrt{a} \}^2.$$

Here $R_1$ and $R_2$ are the gas constants for the unit of weight of the components concerned. For $a_{22} = 0$ this equation passes into [3]):

$$4 \tau \omega^3 = (1-x) \left[ \{ 3\omega - (1-x) \}^2 + \frac{R_1}{R_2} \cdot \frac{b^2_{22}}{b^2_{12}} x (1-x) \right]$$

if we put $\dfrac{T}{Tk_1} = \tau$ , $\dfrac{v}{vk_1} = \omega$. The roots of this equation in

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[1]) Cf. Comm. N°. 96*a*, 96*b*, and 96*c*.

[2]) The quantities $a_{11}$, $a_{22}$, $a_{12}$, $b_{11}$, $b_{22}$, $b_{12}$, etc. relate to the unit of weight, $a_{11M}$, $a_{22M}$ etc. to the molecular quantity.

[3]) For the $\psi$-surface for the molecular quantity and $b_{22M} = b_{11M}$ this equation passes into an equation which is quadratic in $x$; as VAN LAAR Proc. Kon. Akad. van Wet. May '05 p. 36 remarked, the course of the successive spinodal curves may then be found in a simple way by solving those equations.

$\omega$ for definite values of $x$ and $\tau$ have been determined by a graphical way. The figure has been constructed for mixtures for which $R_2/R_1 = {}^1/_2$, $b_{22}/b_{11} = {}^1/_4$ (cf. Comm. No. 96*c*, p. 23 footnote 1).

With reference to Fig. 1 we point out that for $T < T_{km}$ ($= 1.299\ T_{k_1}$) and $> T_{k_1}$ a spinodal curve closed on the side of the increasing $v$'s, and together with it a similar plait, extends on the $\psi$-surface from the side of the small $v$'s. At $T = T_{k_1}$ this plait reaches the side of the least volatile component. At lower $T$ the spinodal curve has two distinct branches, and the plait runs in a slanting direction from the line $v = b$ to the side of the least volatile component [1].

Thus the investigation of mixtures with a gas without cohesion calls attention to a plait that starts from the side of the small volumes, and at lower temperature runs in an oblique direction to the transverse side of the surface, which plait can be distinguished from the transverse and from the longitudinal plaits.

The spinodal curve for $\tau = 1.040$ has a barotropic plaitpoint $P_b$ (see Fig. 1). For $1.299 > \tau > 1.040$ the angle which the tangent to the plait in the plaitpoint makes with the $v$-axis [2] $\theta_{pl} > \frac{\pi}{2}$, for $1.040 > \tau > 1$ is $\theta_{pl} < \frac{\pi}{2}$. The barotropic phenomena for such a plait will be further discussed in a following communication (cf. N⁰. 96*c* p. 22 footnote 1).

In Fig. 2 the course of the plait has been schematically represented for a temperature between the barotropic plaitpoint temperature and the critical temperature of the first component. The —-—-— curves denote the pressure curves, the — -- — curve the spinodal curve, the continuous curve the connode. The straight line $AB$ is the tangent chord joining the coexisting phases $A$ and $B$, $CD$ is the barotropic tangent chord (Comm. N⁰. 96*b*).

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[1] As KORTEWEG, l. c. p. 3 footnote 2, treats the $\psi$-surface in the so-called symmetrical case (c.f. p. 12 footnote 2), the plait described by him shows at lower temperatures another course than the one described by us (cf. p. 3 footnote 2).

[2] Cf. Comm. N⁰. 96*b*.

§ 3. *Limited miscibility of two gases.* For mixtures where as in fig. 2 a plait giving rise to phases *separated by a meniscus* which coexist in pairs, represented in the figure e.g. by $A$ and $B$, while mixtures in intermediate concentrations are not stable, extends on the $\psi$-surface from the side of the small $v$'s at temperatures above the critical temperature of the least volatile component, we shall call not only the phase $B$ a gas phase, for which it is a matter of course, but also the other $A$; so the latter may be called a *second gas phase*, and we may speak of *equilibria between two gaseous mixtures* at those temperatures. That there is every reason to do so in the case treated in § 2 appears already from this, that the reduced temperature of the phase $A$, calculated with the critical temperature of the unsplit mixture with the concentration of $A$, is so high that already through its whole character the phase must immediately make the impression of a gas phase (so a second one).

The shape of the $p$-curves in fig. 2 shows further, how the two coexisting gas phases may be obtained by isopiestic and isothermic mixing, in which nothing would indicate a transition to the liquid state, from the gas phases $M$ and $N$ of the simple substances [1]).

We shall explain in the following § that it is really in accordance with the distinction between gas state and liquid state for binary mixtures in general, when we call $A$ a second gas phase.

§ 4. *Distinction between gas and liquid states for binary mixtures.* It is true that since the continuity of the gas and the liquid states of aggregation has been ascertained, it may be said with a certain degree of justice, that it is no longer possible to draw the line between the two states, but when in the definition of what is to be understood by liquid and what by gas we wish properly to express the difference and the continuity in the character of the heterogeneous region and the homogeneous region and to preclude conclusions [2]) which are irreconcilable with the most obvious conception of phenomena, then the limits allowed for making this definition, are very narrow.

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[1]) Cf. footnote 1 p. 4.

[2]) So THIESEN'S definition, Z.S. für compr. und fl. Gase 1 (1897) p. 86, according to which e.g. strongly compressed hydrogen at ordinary temperatures would have to be called a liquid.

Thus for a simple substance no other distinction will be possible than by means of the isotherm of the critical temperature, and the border curve (connodal curve on GIBBS's surface), which is divided into two branches by the critical state (plaitpoint of the connodal curve), of which the branch with the larger volumes is to be defined as gas branch, that with the smaller volumes as liquid branch[1]). Liquid phases are only those which by isothermic expansion may pass into such as lie on the liquid branch of the connodal curve, and also the metastable [2]) phases lying between the connodal and the spinodal curves, which may be brought on the liquid branch of the connodal curve by isothermic compression [3]).

For binary mixtures the consideration of the $\psi$-surface of VAN DER WAALS leads in many cases to definitions which are just as binding. When discussing this we shall leave out of account the case of solid states of aggregation and three phase equlibria.

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[1]) This is in harmony with the principle of *continuity of phase along the border curve* according to which a change of the character of the phases on a border curve can only occur in a critical point. For substances which at temperatures near the critical one, in states represented by points on, or in the vicinity of that branch of the connodal curve on GIBBS's surface which connects the liquid states at low temperatures with the plaitpoint, should be associated to multiple molecules of which the volume is *greater* than the volumes of the composing molecules together, this principle would admit the possibility that on the liquid branch of the border curve liquid phases should occur with greater volume than the coexisting gasphase. Such simple substances would then show the barotropic phenomenon, till now only found for binary mixtures. There is nothing known that points in the direction of making the existence of such simple substances probable but there can be no more given a reason why it should be impossible.

[2]) The metastable states have not been included in BOLTZMANN's definition Gastheorie II, p. 45.

[3]) We do not accept the principle of the distinction of O. LEHMANN, Ann. d. Phys. 22 (1907) p. 474: "Erst die unterhalb der betrachteten Isotherme liegenden Kurven, welche in ihrem *S*-förmigen Teil unter die Abszissenachse hinunterreichen, entsprechen wahrer (tropfbarer) Flüssigkeit, d. h. einem Zustand der negativen Druck zu ertragen im Stande ist", as depending on the meaning that the existence of capillary surface tension in liquids which can form drops, would presuppose that these liquids can bear external tensile forces, i. e. negative pressures without splitting up (cf. ibid p. 472 in the middle, and p. 475 at the top).

In the first place gas states are all the states on the $\psi$-surfaces on which there are no plaits. As criterion to divide states which belong to the stable or metastable [1] region of $\psi$-surfaces which show plaits, into gas states and liquid states, analogy with the simple substance indicates their relation with the connodal curves of those plaits while for the metastable states the help of spinodal curves is to be called in.

For this first of all the distinction between the two branches of the connodal curve of a plait is required. For in the first place we shall have to give the same name to each of the two branches of a connodal curve separated by one or two plaitpoints throughout its length [2].

Now, on account of the existence of the barotropic phenomenon we cannot simply call gas branch of the connodal curve that at which one of the isopiestically connected states has the smallest density [3]. It is therefore the question to indicate if possible on each branch a state whose nature is already known through the definition holding for simple substances or for those which behave as such when splitting up into two phases. In this different cases are to be distinguished.

For the case that the considered plait [4] extends from one of the side planes $x = 0$ or $x = 1$ over the $\psi$-surface, it follows from the definition of gas phase and liquid phase of a single substance that the branch of the connodal curve from the gas state of the pure substance to the plaitpoint is to be called gas branch, and also that the branch from the liquid phase of the simple substance to the plaitpoint is to be called liquid branch. The gas branch and the liquid branch of the spinodal curve may be distinguished in the same way as those of the connodal curve.

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[1] It follows from the nature of the case that unstable states have not to be considered here.

[2] Cf. p. 8 footnote 1.

[3] Even if we wish to leave gravity out of account, and pay only attention to the molecular volume of the phase, the barotropic phenomena have yet called attention to the possibility that we may find the gas volume first larger and then smaller than the liquid volume when passing along the same connodal curve.

[4] The case of the two plaits at minimum critical temperature is comprised in this.

Let us restrict ourselves for the present to the distinction of gas and liquid in this case. In the first place we make use for this purpose of the isomignic (Comm. N$^0$. 96*b*) compression and expansion. Every phase which cannot be brought on the connodal curve through this operation, or if it can, comes on the gas branch, will have to be called a gas phase, every phase which is made to lie on the liquid branch through isomignic expansion is a liquid phase. Besides the phases lying between the connodal and the spinodal curves which isomignically may be brought on the liquid branch of the connodal are metastable liquid phases.

Besides the isothermic and isomignic compression without splitting there is another operation already mentioned in § 3, which may help us to form an opinion about the similarity of different phases, viz. the isopiestic and isothermic mixing [1]). With regard to this phases which have been obtained by isopiestic admixing without splitting from phases of which it has been ascertained that they are to be called liquid phases, must be called liquid phases until in another way (e. g. because no splitting takes place with isomignic compression and expansion) they have been proved to have passed into gas phases [2]).

Proceeding to the case that the plait from higher temperature appears as a closed plait on the $\psi$-surface, as long as the plaitpoint which first comes into contact with the side with decrease of temperature, has not yet come into contact, and with decrease of temperature the plait has not yet reached a mixture which on splitting behaves as a simple substance, and for which the distinction in liquid state and gas state is therefore fixed, we shall have to consider that branch of the connodal curve on the side of this plaitpoint, which passes into that of the gas phase at lower temperature, as belonging to the ordinary gas phase, whereas the branch which passes into the liquid branch at lower temperature may be looked upon as a *second gas phase*, and we are the more justified in doing so as the temperature should lie further above the critical temperatures of the unsplit mixtures belonging to the phases lying on them.

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[1]) With the continuous isothermic and isopiestic mixing of two similar phases *a* and *b* the case may present itself (divided plait in the case of minimum crit. temp.), that an intermediate phase *c* of the other kind is obtained. So in general we cannot conclude to the similarity of *c* from the isothermic and isopiestic mixing of similar *a* and *b*.

[2]) This criterion is particularly of application to the retrograde condensation 2nd kind. For then phases on the connodal curve between the plaitploint and the critical point of contact are liquid phases, phases on the *p*-curve through the plaitpoint and phases with the same *x* as the critical point of contact just the transitions to gas phases. The phases within the triangle bounded by these two lines and the connodal curve are also to be considered as liquid phases.

Here we abstract from the small uncertainties which would be caused in these definitions when capillarity ought to be taken into account.

Whereas in the case, that at a temperature comparatively little lower also the other side of the $\psi$-surface is reached by the originally closed plait, the difference of the second gas phase with a liquid phase is still not very conspicuous, this may become very clear for the case of § 2, to which we have now got at last, that viz. with decreasing temperature a plait comes from the side $v = b_x$ on the $\psi$-surface, and the plait appears for the first time as longitudinal plait. Now we may again call $PBDF$ the branch of the first gas phase, $PACE$ the branch of the second gas phase. It will certainly be obvious to speak of gas phases when *all* the parts of the plait are found above the critical temperatures of the unsplit mixtures, and we shall decidedly *have* to speak of two gas phases, when the second branch of the connodal curve is intersected all over its length by isomignic lines on which beyond this plait no splitting up occurs, or if it is at most touched by one of them in the point $v = b$. For then it is beyond doubt that the final point of that branch must be called a gas phase.

Possibly also phases between the isomignic line of the critical point of contact, the line $v = b_x$ and the second gas branch belong to the second gas phase.

§ 5. *The surface of saturation for equilibria on the gas-gasplait.* In fig. 3, 4 and 5 the sections $T = \text{const.}$ of the $p, T, x$-surface of saturation for equilibria on the gas-gasplait have been schematically drawn for a mixture in which one component is a gas without, or almost without cohesion, in fig. 3 and 4 for temperatures higher than the critical temperature of the first component, in fig. 5 for this last temperature.

In these figures too the division of a gas phase into two gas phases, and the transition of a part of the gas region into the liquid region at $T = T_{k_1}$ is clearly set forth. The — — — — curve is the locus of the plaitpoints.

In a following communication, in which the properties of the $\psi$-surface for such mixtures will be further discussed, $T$, $x$-sections etc. will be drawn of this surface of saturation. At the same time it will then have to appear in how far *retrograde* unmixing of a phase into two other phases is to be expected.

That one of these phases may be called a second gas phase, appears in § 4.

§ 6. *On the conditions which must be fulfilled that limited miscibility of two gases may be expected.* Now that it has appeared that on the suppositions mentioned in § 2 for mixtures in which one component is a gas without cohesion with molecules with extension, limited miscibility might be expected in the gas state, the question rises whether this phenomenon is also to be expected for mixtures with a gas of feeble cohesion. As on the said suppositions no maximum critical temp. is to be expected, this will be the case when $T_{km} > T_{k_1}$ is found [1]. We have treated this question by the aid of the $\psi$-surface for the molecular quantity (cf. § 2). We arrive then at the equations developed by VAN DER WAALS Contin. II p. 43. The condition that $T_{km} > T_{k1}$ is [2]:

$$\{b_{22M}/b_{11M} - \sqrt{a_{22M}/a_{11M}}\}^2 > \frac{4}{27}\, b^3{}_M/b^3{}_{11M} \cdot \frac{1}{x_M(1-x_M)}$$

in which $b_M$ and $x_M(1-x_M)$ follow from the equations given by VAN DER WAALS loc. cit. We find from this [3]) $T_{km} > T_{k1}$,

| | |
|---|---|
| for $b_{22M}/b_{11M} = 2$ , | if $a_{22M}/a_{11M} < 0.58$ |
| $1$ | $0.053$ |
| $1/2$ | $0.0037$ |
| $1/4$ | $0.00023$ |
| $1/8$ | $0.000015.$ |

It appears on investigation that only for few pairs of substances the ratios of the *a*'s and *b*'s ¹) will be able to satisfy the condition. The still unknown relations between *a* and *b* for a same substance, to which we alluded in § 1, and from which ensues that in general substances with small *a* also possess a small *b*, and that as a rule large *b* goes together with large *a*, seem to prevent this. He, which with a *b* which is still not very small compared with $H_2$ possesses a very small *a*, so feeble cohesion, and $H_2O$, which taking the value of *a* into consideration, has a comparatively small *b*, so a molecule of small volume, constitute exceptions to this general rule which are favourable for the phenomenon treated here.

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[1]) Whether limited miscibility in the gas state may also occur if $T_{km} < T_{k_1}$ in certain cases and at suitable temperatures, will be discussed in § 7.

[2]) For the symmetrical case ($b_{11M} = b_{12M} = b_{22M}$, $a_{11M} = a_{22M}$ but $\gtrless a_{12M}$) KORTEWEG treated this condition l. c. pag. 3 footnote 2, p. 335).

[3]) For $b_{22M}/b_{11M} = 1/8$ e.g. we find also $T_{km} > T_{k_1}$ for $0.125 > a_{22M}/a_{11M} > 0.061$ These cases are to be discussed further.

If for He -- $H_2$ : $b_{22M}/b_{11M} = {}^1/_2$, and $a_{22M}/a_{11M} = {}^1/_{175}$ (Comm. No. 96*c*, p. 23 footnote 1), $T_{km} < T_{k1}$ must be expected on the above suppositions. Also for helium-argon and helium-oxygen e.g. the same thing must be expected. Most likely the ratios are more favourable for mixtures of helium and neon ²) than for those of helium and hydrogen (cf. § 8).

For mixtures of helium and water the ratios for the above assumed $a_{He}$ and $b_{He}$ are such that for them limited miscibility in the gas state is to be expected, if the suppositions mentioned in § 2 are to be applied (cf. § 8).

The coefficients of viscosity and of conduction of heat (cf. Comm. No. 96*c*, p. 23 footnote 1) admit a value of $b_{He}$ which is still somewhat though only little higher; this might render it possible to realize the said phenomenon perhaps also for the other pairs of substances mentioned, especially when we bear in mind that its appearance is not excluded for $T_{km} < T_{k1}$ (cf. p. 12 footnote 1).

The experimental investigation of these mixtures has been taken in hand in the Leiden Laboratory.

(March 30, 1907).

§ 7. *The shape of the spinodal curves and of the plaits for the case that the molecules of one component exert some, though still feeble attraction.* With very small value of the mutual attraction

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¹) See e. g. KOHNSTAMM, LANDOLT-BÖRNSTEIN-MEYERHOFFER's Physik. Chem. Tabellen.

²) Cf. RAMSAY and TRAVERS, Phil. Trans. A. 197 (1901) p. 47 for data concerning refractive power and critical temperature of neon.

$a_{12}$ of the molecules of the two components, in connection with the feeble attraction $a_{22}$ of the molecules of one component inter se, the spinodal curve will with decreasing temperature extend more and more on the $\psi$-surface as in Pl. I fig. 1 from the side of the small $v$'s, come into contact with the line $x = 0$ at $T = T_{k_1}$, and then cross from the line $v = b$ to the side $x = 0$ in two isolated branches [1]) We leave here out of account what takes place at lower temperatures when the spinodal curve approaches and reaches the side $x = 1$ too.

To examine what shape the spinodal curve can have with greater attraction of the most volatile component, we shall avail ourselves of the suppositions introduced in § 2 and also applied in § 6 concerning the equation of state and the quantities $a_{12}$ [2]) and $b_{12}$. In the net of spinodal curves for a given pair of substances 2 double points may then occur, belonging to the spinodal curves for different temperatures. The values of $x$ for these are determined by the equation:

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[1]) Here $\frac{dT_{xpl}}{dx} > 0$ for $x = 0$. We see here that VERSCHAFFELT'S conclusion (Suppl. N$^0$. 11 p. 11) concerning the maximum temperature in the plaitpoint curve for mixtures, for which the component is indicated by a point from the region $OHK$ (see fig. 2 l. c.) must be supplemented by the possibility that the branch of the plaitpoint curve starting from the first component, goes to infinite pressures. A same remark may be made regarding the conclusion of VERSCHAFFELT § 9 l. c. (cf. Suppl. No 19, errata ad addenda to Suppl No. 11).

[2]) In this first investigation of what may be expected for mixtures of helium, with a view of forming some opinion as to the conditions under which the experiments for this purpose are to be made, we put (§ 2), $b_{12M} = \frac{1}{2}(b_{11M} + b_{22M})$, $a_{12M} = \sqrt{a_{11M}\, a_{22M}}$ (cf. Comm. Suppl. No. 8, p. 9) in the calculations, no data concerning $a_{12}$ and $b_{12}$ for those mixtures being available as yet. Also VAN DER WAALS (Proc. Kon. Acad. v. Wet. Amsterdam Febr. '07, p. 630) assumes that as a rule $a_{12M} < {}^1/_2\,(a_{11M} + a_{12M})$. It will be necessary for a complete survey concerning the different possibilities to make also other suppositions about $a_{12M}$ (cf. VAN DER WAALS l.c., KOHNSTAMM ibid. p. 642), at the same time taking into account that $a$ and $b$ are not independent of $v$ and $T$, at least not both (cf. VAN DER WAALS, Proc. Kon. Acad. v. Wet. Amsterdam Sept. '05 p. 289) and that they may only be put quadratic functions of $x$ by approximation.

If also for mixtures with very small $a_{22}$, $a_{12M}$ might be $< \sqrt{a_{11M}\, a_{22M}}$ (cf. KOHNSTAMM l.c. and Suppl. No. 16 p. 11) the phenomena of limited miscibility under discussion might still be sooner expected.

$$\frac{x_M}{1-x_M} = \frac{\sqrt{a_{11M}}}{\sqrt{a_{22M}}} \cdot \frac{3\, b_{11M} \sqrt{a_{22M}} \mp 2 b_{11M} \sqrt[4]{a_{11M}\, a_{22M}} - b_{22M} \sqrt{a_{11M}}}{-b_{11M} \sqrt{a_{22M}} \mp 2 b_{22M} \sqrt[4]{a_{11M}\, a_{22M}} + 3 b_{22M} \sqrt{a_{11M}}}. \qquad (1)$$

For very small $a_{22}$ we find from this two double points with $x > 1$, so not belonging to that part of the $\psi$-surface which can denote phases of mixtures. Of these two double points that for which the lowest signs hold, passes trough infinity for increasing $a_{22}$, and then approaches the line $x = 0$ on the other side of the $\psi$-surface. This line is reached for:

$$\sqrt[4]{a_{22M}/a_{11M}} = \frac{1}{3}\left\{-1 + \sqrt{1 + 3\, b_{22M}/b_{11M}}\right\} = m_1 \quad . \ (2)$$

With increasing $a_{22}/a_{11}$ the double point, which appears to be a node ($\times$) for this region, approaches the line $v = b$, which line is reached for [1]):

$$\sqrt[4]{a_{22M}/a_{11M}} = -(1 - b_{22M}/b_{11M}) + \sqrt{1 - b_{22M}/b_{11M} + (b_{22M}/b_{11M})^2} = \\ = m_2 \ (3)$$

In the further discussion we assume $b_{22M} < b_{11M}$ [2]).

So if the mutual attraction of the molecules of the most volatile component and those of the other in connection with the attractions inter se attains a certain value — on the assumptions made for the calculations for $m = \sqrt[4]{a_{22M}/a_{11M}} = m_1$ — the spinodal curve for $T = T_{k_1}$ will no longer touch the side in $K_1$ (cf. fig. 1 Pl. I), but it will have a double point there, in which the two branches of the spinodal curve intersect each other and the line $x = 0$ at an angle. In this case the critical temperature of the least volatile component is not changed in first approximation by small quantities of admixtures.

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[1]) The *two* criteria for the case $b$), the course of the plaitpoint curve being from $K_1$ to $K_m$ (see p. 22), are in the same time the criteria that a minimum plaitpoint temperature occurs (supposing $b_{22M} < b_{11M}$). As VAN LAAR points out (Proc. Kon. Acad. Amst., May '07, p. 45, appendix), the first-mentioned condition corresponds with a condition for the occurrence of a minimum plaitpoint temperature, derived by him Proc. Kon Acad. Amst., Dec. '05, p. 581 (and VERSCHAFFELT, Suppl. No. 11, p. 11).

[2]) For $b_{22M} > b_{11M}$ the other double point comes from the side $x = 1$ on the $\psi$-surface for a value of $a_{22M}/a_{11M}$ smaller than $m_2^4$. As probably this case does not present itself for the pairs of substances with small $a_{22}/a_{11}$ known to us, we shall not discuss it.

With greater attraction of the most volatile component — on the suppositions mentioned for $m_1 < m < m_2$ — a certain spinodal curve will have a double point on the $\psi$-surface. This will lie the nearer to the side of the small $v$'s, the more the attraction of the most volatile component increases. With a certain value of the attraction — $m = m_2$ — the spinodal curve reaches the line $v = b$ with a double point, with greater attraction the spinodal curve will proceed from $x = 0$ on the $\psi$-surface with decreasing $T$, and touch the line $v = b$ at $T = T_{km}$. On the suppositions mentioned for $b_{22M}/b_{11M} < {}^{16}/_{21}$ the contact with the line $v = b$ will here, at least first after $m$ exceeding $m_2$, take place at temperatures $> T_{k2}$, for $b_{22M}/b_{11M} > {}^{16}/_{21}$ at $T < T_{k2}$, so that in the latter case the spinodal curve comes first into contact with the line $x = 1$.

In the first case ($b_{22M}/b_{11M} < {}^{16}/_{21}$) a plait will come from $x = 0$ and at lower $T$, whereas for larger $m$ a branch plait directed to the side $x = 1$ may develop : if $m < m_2$ it will be united through an homogeneous double plaitpoint (KORTEWEG, Archiv. Néerl. 24 (1891) p. 70), with a plait coming from $v = b$ to a plait that crosses from one side to the other ; if $m > m_2$ it will pass into such a plait by contact with $v = b$.

In the second case the plait which comes from $x = 0$ will again unite with one coming from $v = b$ for smaller $m$ ; for larger $m$ a branch plait will have developed before this union takes place or before the spinodal curve touches the line $v = b$.

The shape of the spinodal curve for these cases with always greater attraction of the most volatile component, where we shall have to consider three phase equilibria, need not be discussed for the present, as they do not belong to the case of a component with feeble attraction ¹).

For some values of $b_{22M}/b_{11M}$ table I gives the values $a_{22M}/a_{11M} = m^4$, calculated from the equations (2) and (3) If we compare with this

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¹) Cf. moreover VAN LAAR, Arch. TEYLER (2) 10 (1906), Proc. Kon. Acad. v. Wet. Amst. Sept. '06 p. 226.

the values of $a_{22M}/a_{11M}$ for which $T_{km} = T_{k1}$ (§ 6), we see that they really lie between those calculated here

The shape of the spinodal curves for a case, in which $m_1 < m < m_2$, has been represented on plate II fig. 1, for the $\psi$-surface of the unit of weight (cf. § 2), with the relations and data assumed in § 2, except that $a_{22}/a_{11} = 0.00049$ (or $a_{22M}/a_{11M} = 0.00196$).

TABLE I.

| $b_{22M}/b_{11M}$ | $m_1^4$ | $m_2^4$ |
|---|---|---|
| $^1/_2$ | 0.0014 | 0.0179 |
| $^1/_4$ | 0.000134 | 0.000527 |
| $^1/_8$ | 0.000011 | 0.000022 |

The plait extending on the $\psi$-surface from $v = b$ for a temperature $> T_{k1}$, will have to be considered as a gas-gasplait according to § 4 (cf. § 6). Also a similar plait for $T < T_{k1}$, if the connodal curve is not touched by an isomignic line, and is nowhere cut by an isomignic line which intersects the connodal curve of the plait coming from $x = 0$ [1]. According to § 4 we shall be justified in considering also the plait lying on the side of the small $v$'s for $T_{k1} > T > T_{dpl}$ (temperature for which the double plaitpoint considered occurs) as gas-gasplait, if the temperature is above the critical temperatures of the unsplit mixtures for all parts of that plait. That there can be some reason for doing so, appears when we calculate the reduced temperature for the double plaitpoint for some cases, e.g. for the ratios $b_{22M}/b_{11M}$ and the $m_2$ belonging to it, mentioned in Table I.

Putting $b_{22M}/b_{11M} = n$ the double plaitpoint temperature is determined by:

$$T_{dpl}/T_{k1} = \frac{27}{4} m (1 + m) \frac{(n - m^2)^2}{(n + m)^3}$$

and

$$v_{dpl}/v_{k1} = \frac{2}{3} \frac{m}{(1+m)^2} \cdot \frac{(n+m)^2}{m(2-m) - n(1-2m)}$$

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[1] Here it appears that a gas-gasplait can occur also if $T_{km} < T_{k_1}$, and for temperatures $T < T_{k_1}$ with $T_{km} > T_{k_1}$ (cf. p. 12 note 1 and p. 13).

So for the case represented on Plate II fig. 1 we find:

$$x_{dpl} = 0.587,\quad T_{dpl}/T_{k_1} = 0.996,\quad T_{dpl}/T_{kx} = 2.17.$$

(May 24, 1907.)

§ 8. *On the temperatures and the pressures on the gas-gasplait* [1]). In order to form a provisional opinion as to the experimental conditions which must be satisfied that limited miscibility in the gas state may be observed, and to be able to derive what pairs of substances must be considered suitable for this purpose, it is desirable to examine for some cases what temperatures and pressures occur on the gas-gasplait [2]). In the case (§ 2. March '07) of a component without cohesion [3]) or almost without cohesion ($m < m_1$, see § 7), the gas-gasplait will occur for all temperatures between the critical temperature of the less volatile component and the critical temperature of complete miscibility [1]). Its pressures will then be larger than the critical pressure of the least volatile component. If the suppositions mentioned in § 2 might be applied for this, and the values of $a_M$ and $b_M$ for He might be borrowed from Comm. N⁰. 96$c$, p. 23 footnote 1, so that $a_{MHe} = {}^1/_{175}\, a_{MH_2} = 0.0000024$ and $b_{MHe} = {}^1/_2\, b_{MH_2} = 0.00044$, this case would be realized for mixtures of He and water [2]). Then we should find $T_{km} = 1.056\ T_{k_1}$, so that the gas-gasplait would occur over a range of temperature of 36° above 365° C., and at pressures above 195 à 200 atms.

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[1]) In Proc. Kon. Akad. Amsterdam May '07, p. 34—46, VAN LAAR published some remarks concerning the priority of several results we gained in the former §§. Since VAN LAAR, after our defence inserted in §§ 8 and 9 of the original of this paper, in Proc. Amst. Sept. '07 p. 238—239 completely acknowledges our priority, we have in this translation omitted the relating personal parts.

[2]) Also in the case of a three-phase-equilibrium, as e.g. in the system water-ether, our terminology with regard to the distinction between gas and liquid agrees with that used by VAN DER WAALS. According to what has been said about this distinction in § 4, for a three phase equilibrium of a system of the type water-ether, of which we denote the phase with smallest density by $\alpha$, that of the two phases with greater density which is rich in the most volatile component (ether) by $\beta$, and finally that of the latter which is rich in the least volatile component (water) by $\gamma$, the phase $\gamma$ *must* be called liquid as belonging to the liquid branch of the connode, just as the phase $\alpha$ *must* be called gas phase; whether the phase $\beta$ is to be called liquid or gas, is not determined by the principle of the continuity of the phase along the connode; if the reduced temperatures at which this phase appears, are taken into account, also the last mentioned phase will be called liquid for the system ether-water in accordance with what has been said in § 4.

[3]) The second branch of the plaitpoint curve in Fig. 1 §2, has there ($a_{22} = 0$) contracted to a point $x = 1$, $v = b_{22}$. It is true that in the case of our § 7 (Plate II) a second branch of the plaitpoint curve occurs, but as has been explicitly stated there (p. 14 and p. 16), that we did not discuss the spinodal curves at the lower temperatures at which this branch of the plaitpoint curve makes its influence felt, referring inter alia with a view to these temperatures to VAN LAAR'S papers.

In the case that the molecules of the least volatile component act on each other feebly, but still exert such an attraction that a double plaitpoint [3]) occurs in the net of the spinodal curves, the pressure in this plaitpoint and its temperature in connection with the critical temperature of complete miscibility give important indications as to the pressures and temperatures of the gas-gasplait.

In table II these data, calculated for the case that the suppositions mentioned in § 2 might be applied, have been given for some helium mixtures [4]). $T_{km}$ has here been calculated according to VAN DER WAALS Cont. II, p. 43 (cf. § 6), $T_{dpl}$ according to the formula mentioned in § 7, $p_{dpl}$ from the equation of state with the just mentioned $T_{dpl}$ and the $v_{dpl}$ also represented in formula in § 7 [5]).

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[1]) As mentioned in § 1 this idea was introduced by VAN DER WAALS, who also gave the formulae for the calculation of this temperature (VAN LAAR calls it „third critical temperature").

[2]) The $a_M$ and $b_M$ for water have been borrowed from LANDOLT-BÖRNSTEIN-MEYERHOFFER's Physik. Chem. Tabellen. Cf. Suppl. No. 16 p. 4 footnote 4.

[3]) The appearance of a double plaitpoint near $K_m$ was already observed by VAN LAAR (Proc. Kon. Acad. Amst. May. 1905 p. 42). The detaching of a longitudinal plait at high temperatures, which leaves the $\psi$-surface with its open side turned to $v = b$, follows immediately (see Proc. Kon Acad. Amst. April '07 p 848 footnote) from the general considerations and calculations of VAN DER WAALS Cont. II § 19 sqq. and VAN DER WAALS' diagram in Zittingsverslag Kon. Akad. Nov. 1894 p. 133, when the case ($a$) cf. § 9 does not occur.

[4]) For the classification of the helium mixtures according to a later estimation of the critical temperature of helium, see Suppl. No. 16 p. 4 footnote 4.

[5]) In a following Communiation (cf. Suppl. No. 16 p. 6 footnote 2) we will indicate the developments which led us to the explicit expressions for the double plaitpoint mentioned pp. 15 and 17.

TABLE II.

| Pair of substances | $T_{km}/T_{k_1}$ | $T_{dpl}/T_{k_1}$ | $T_{dpl}/T_{kx}$ | $p_{dpl}/p_{k_1}$ |
|---|---|---|---|---|
| Hydrogen-helium . . | 0.933 | 0.915 | 4.44 | 41.6 |
| Oxygen-helium . . | 0.962 | 0.957 | 8.64 | 61.3 |
| Argon-helium . . . | 0.970 | 0.962 | 7.90 | 64.5 |
| Neon-helium . . . | 1.007 | 0.961 | 3.72 | 18.8 |
| NO-helium . . . . | 1.031 | 0.991 | 3.76 | 13.1 |
| $NH_3$-helium . . . . | 1.009 | 0.969 | 6.20 | 25.2 |
| $H_2S$-helium . . . . | 0.972 | 0.970 | 13.79 | 171 |
| $CO_2$-helium . . . . | 0.9540 | 0.9536 | 15.89 | 1045 |

The reduced temperature of the double plaitpoint $T_{dpl} / T_{kx}$, mentioned in this table, gives an idea in how far the phases in its neighbourhood behave as compressed gas-phases.

The values of $a$ and $b$ of the different components have been borrowed from KOHNSTAMM, LANDOLT-BÖRNSTEIN-MEYERHOFFER'S Physik. Chem. Tabellen; for those of helium see above; for neon we have made use of the ratio of its refractive power ¹) to that of helium according to the determinations of RAMSAY and TRAVERS ²),

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¹) HAPPEL, Habilitationsschrift Tübingen 1906, p. 30, found that the refractive power for argon, crypton and xenon would yield values for $b$ which greatly deviate from the $b$'s derived from the critical data. When according to the principle of the corresponding states (cf. HAPPEL loc. cit. p. 31. note 1) we compare the ratios of the refractive powers for these gases with those of their critical volumes (derived from $p_k$ and $T_k$) the deviations are far less considerable. So with regard to this property, these one-atomic gases form a group, just as is the case with the bi-atomic and with a great many more-atomic substances (GUYE, Journ. de phys. (2) 9 (1890) p. 312).

²) RAMSAY and TRAVERS, Phil. Trans. A197 (1900) p. 81. Yet we must remark that when comparing this ratio for helium and argon according to RAMSAY and TRAVERS with the ratio of $b_{He}$ according to our estimation and $b_A$ ($b$ for argon) derived from $p_k$ and $T_k$, we should find an important deviation (cf. note 1). Also in view of this the data concerning mixtures of helium and neon are very uncertain.

and of the estimation concerning the critical temperature by TRAVERS, SENTER and JAQUEROD [1]).

It appears from table II that when the gas-gasplait can make its appearance, the range of temperature within which this is the case (between $T_{km}$ and $T_{dpl}$), on the mentioned suppositions is small for most of these pairs of substances, for some even exceedingly narrow.

For the pressures on the gas-gasplait higher values than $p_{dpl}$ will have to be expected as a rule. Thus it appears from table II that these pressures become very high, if the circumstances are not very favourable.

It would have a very favourable influence on the circumstances of temperature and pressure at which limited miscibility in the gas state might be observed, if it should prove that for mixtures of helium with another gas $a_{12M}$ is smaller than is expressed by $\sqrt{a_{11M}\ a_{22M}}$ [2]).

### § 9. *Conclusion* [3]).

The different plaits considered in this paper may be summarized as follows.

Applying the equations laid down by VAN DER WAALS with regard to the spinodal curve in Cont. II, § 19 sqq., transferred to the $\psi$-surface for the unit of weight, to the case that one of the components is a gas without cohesion [4]) with molecules which have extension, we arrive on the suppositions [5]) mentioned in § 2 at a *plait which starts from the side of the small volumes, comes into contact with the line $x = 0$ at a certain temperature, and crosses in a slanting direction from $v = b$ to the side $x = 0$ at lower temperature* (§ 2, March '07).

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[1]) TRAVERS, SENTER and JAQUEROD, Phil. Trans. A 200 (1902) p. 177. Their views, however, on a connection between atomic weight and critical temperature lead to an unlikely result for the critical temperature of helium.

The determinations of isotherms of neon by RAMSAY and TRAVERS, loc. cit. have been of as little use to us as those of helium for the determination of $a$ and $b$ (different particulars in the course of the isotherms of the one-atomic gases given by these scientists in plate 2 loc. cit. do not seem very probable to us).

[2]) Cf. p. 14 note 2, and VAN DER WAALS Proc. Kon. Akad. Amst. April '07

[3]) p. 831. See also Suppl. No. 16 p. 11. Cf. p. 18 footnote 1.

[4]) This investigation was announced in Comm. No. 96*b*, Dec. '06 p. 502.

[5]) When we were not allowed to put $\frac{\partial^2 b}{\partial x^2} = 0$ for and in the immediate neighbourhood of $v = b$, as we did (cf. VAN DER WAALS Cont. II p. 42), the spinodal curve will always be closed towards the side $v = b$ as VAN DER WAALS observes l.c. and Proc. Kon. Akad. Amst. '07 p. 848. It is then to be expected

At decreasing temperature this plait shifts over the $\psi$-surface in such a way that the plaitpoint curve, for which VAN LAAR has given the course, cf. p. 3, footnote 1, runs continuously from the critical point of complete miscibility (VAN DER WAALS l. c.) to the critical point of the less volatile component.

It is on a plait of this kind that for temperatures above the critical temperature of the least volatile component limited miscibility in the gas state mentioned in § 3 sqq. occurs.

The different forms of plaits which may occur with $a_{22} > 0$, but still small, as is to be expected for mixtures with helium, may be classified as follows.

For the case of the plaitpoint curve running from $K_1$ to $K_m$ (called type I by VAN LAAR) 3 cases are to be distinguished (§ 7, March '07): *a*) that with falling temperature the plaitpoint gets from $K_m$ on the $\psi$-surface, and proceeds regularly towards $K_1$; *b*) that with falling temperature a plaitpoint coming from $K_m$ and one coming from $K_1$ unite to a double plaitpoint [1]; *c*) that the plaitpoint gets from $K_1$ on the $\psi$-surface and proceeds regularly towards $K_m$ (without double plaitpoint with minimum plaitpoint temperature). The conditions for the occurrence of these cases were defined by us by means of the equations (2) and (3) of p. 15. From this appeared that with very feeble attraction the case *a*) occurs, with greater attraction the case *b*), whereas with still greater attraction case *c*) occurs (supposing the system to belong to type I).

The course of the temperature along the plaitpoint curve for the different cases treated here, has been drawn in Pl. II fig. 2,

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at least for small $\frac{\partial^2 b}{\partial x^2}$, that the plait in question makes its appearance for the first time at a maximum plaitpoint temperature, and for the rest extends to the large $v$'s in the same way as the plait described here (cf. KORTEWEG l. c. p. 3 footnote 2, p. 337).

[1] The case *b*) was described by VAN LAAR (cf. p. 16) chiefly with regards to the treatment of what takes place at lower temperatures, when three-phase-equilibria occur.

where $\tau = T_{pl}/T_{k_1}$: curve $a$ refers to the $\psi$-surface treated in § 2 (case $a$), $b$ to that treated in § 7 (case $b$), $c$ to the $\psi$-surface which will be treated in Suppl. No. 16 § 2 (case $c$). The $\tau$, $x$-curves for the case ($a$) are limited in fig. 2 by the curve $a$, for which $m = 0$ (cf. § 2) and by the curve $m = m_1$ (cf. § 7), those for the case ($b$) by the curves $m = m_1$ and $m = m_2$ (cf. § 7). The curve $dpl$ is the locus of the minima in the curves $b$ and gives so the temperature for the double plaitpoint (cf. p. 17). The vertical line refers to the $x$ of $K_m$, which as depending only on $b_{22}/b_{11}$ is the same for the different $\psi$-surfaces treated. [This alinea was added in this reprint].

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

## Supplement No. 16

## to No. 97–108.

**Dr. H. KAMERLINGH ONNES and Dr. W. H. KEESOM.**
"Contributions to the knowledge of the $\psi$-surface of VAN DER WAALS. XVI. On the gas phase sinking in the liquid phase for binary mixtures in the case that the molecules of one component exert only a feeble attraction". *(With a plate.)*

*(Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam,* **28 September 1907**, p. 243–245).

EDUARD IJDO — PRINTER — LEIDEN.

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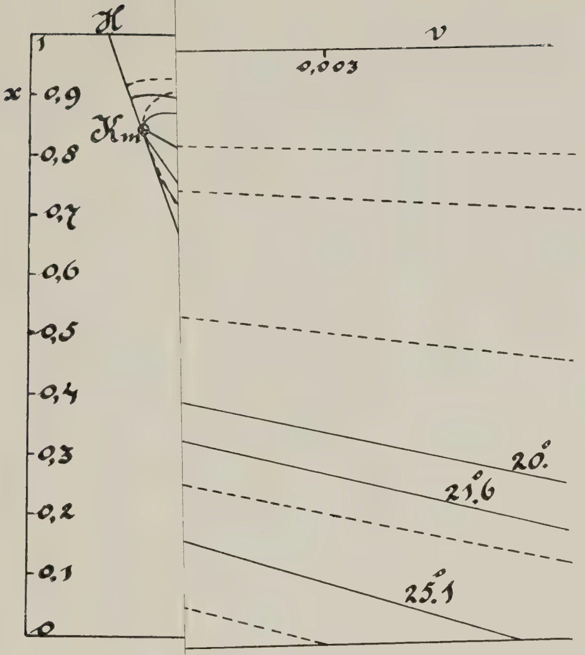

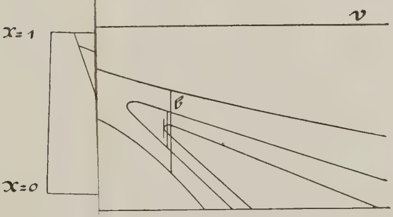

Fig. 3.

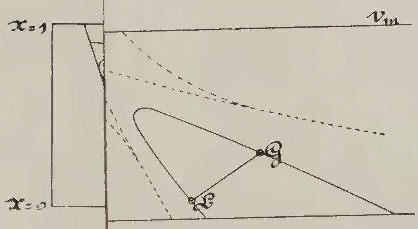

Fig. 7

Communica

Dr. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. "Contributions to the knowledge of the $\psi$-surface of VAN DER WAALS. XVI. On the gasphase sinking in the liquid phase for binary mixtures in the case that the molecules of one component exert only a feeble attraction."

PLATE I.

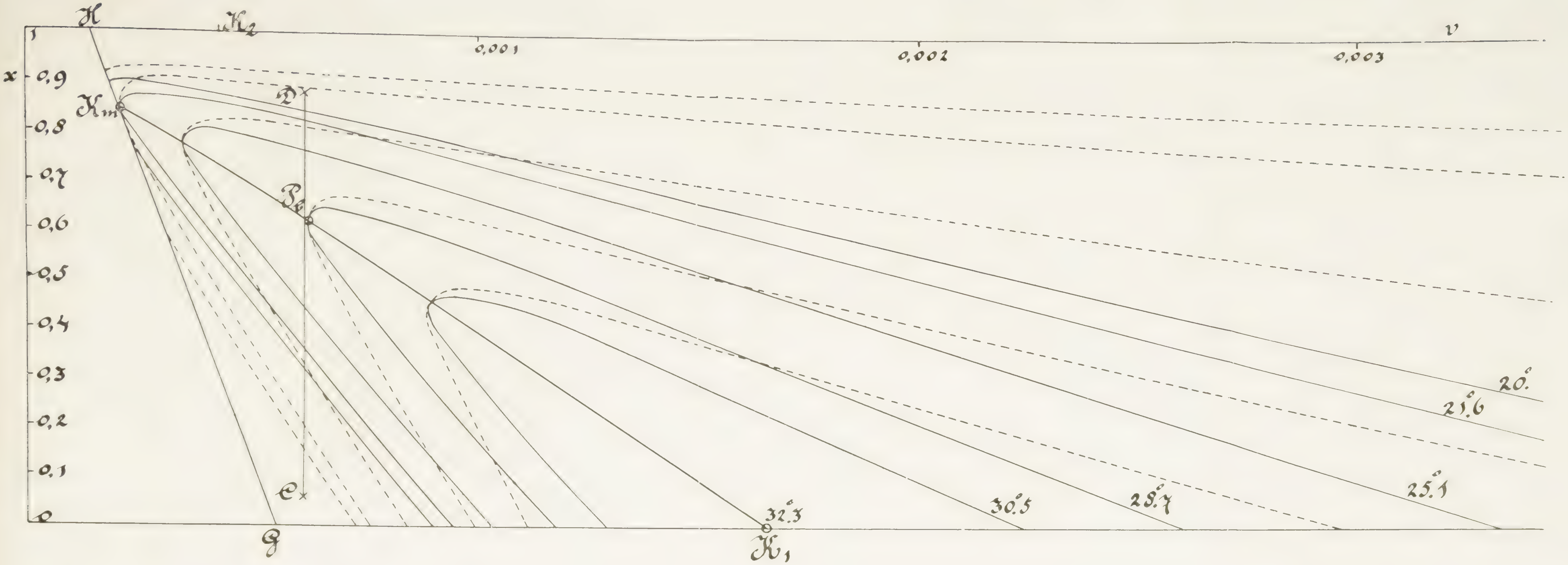

Fig. 5.

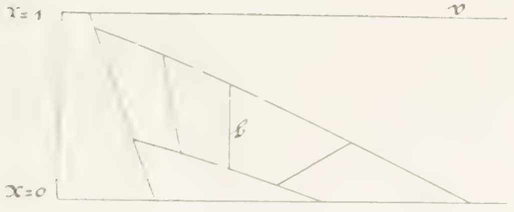

Fig. 1

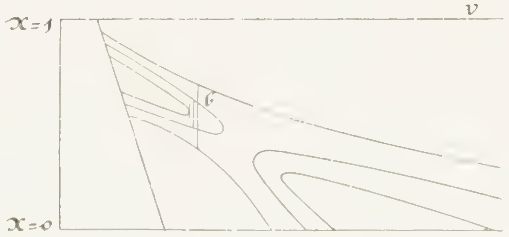

Fig. 2.

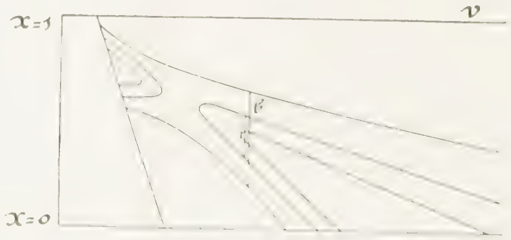

Fig. 3

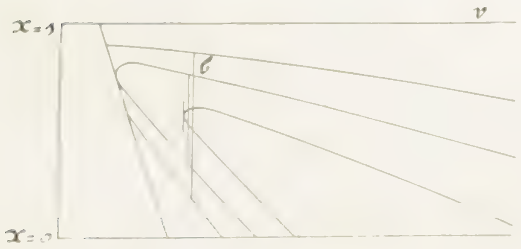

Fig. 4.

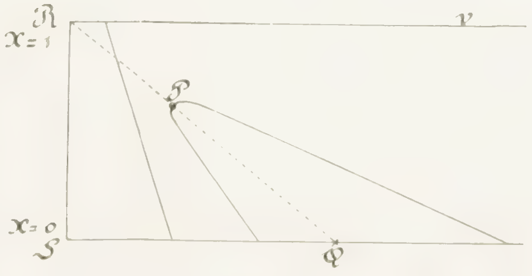

Fig. 6.

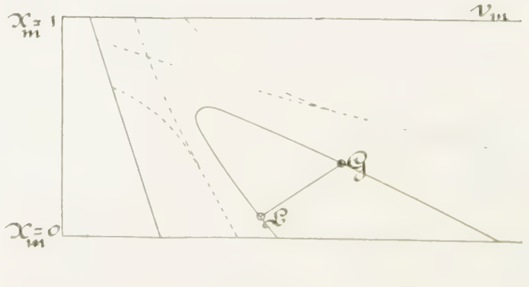

Fig. 7

**Dr. H. KAMERLINGH ONNES and Dr. W. H. KEESOM.** "*Contributions to the knowledge of the $\psi$-surface of* VAN DER WAALS. XVI. *On the gas phase sinking in the liquid phase for binary mixtures in the case that the molecules of one component exert only a feeble attraction.*"

## § 1. *Introduction.*

In Comm. N⁰. 96*b*, Dec. 1906, a gas phase sinking in a liquid phase [1]), the barotropic phenomenon, was treated for binary mixtures for a gas-liquidplait, which crosses the $\psi$-surface as a transverse plait at lower temperature. Then the treatment for temperatures, at which the appearance of a longitudinal plait brings about a disturbance, was deferred to a later communication. Moreover, more special cases, as the appearance of minimum or maximum critical temperature or minimum or maximum pressure of coexistence, were left out of consideration, and the discussion was restricted to the case that retrograde condensation of the first kind occurs.

When for binary mixtures the conditions for the sinking of a gas phase in a liquid phase were treated in Comm. N⁰. 96*c*, Dec. '06 and Jan. '07, it appeared in the first place that at least if the hypotheses mentioned there are valid, and pairs of substances are found with proper $a_{22\,\mathrm{M}}/a_{11\,\mathrm{M}}$, $b_{22\,\mathrm{M}}/b_{11\,\mathrm{M}}$ and $M_2/M_1$ the theory of VAN DER WAALS's $\psi$-surface leads us to expect that barotropic plaitpoints 1) will occur 2). Further that for mixtures with certain ratio $v_{k2}/v_{k1}$ for not too large $T_{k2}/T_{k1}$ (from 0 up to a certain value, see Table I loc. cit. p. 24) only one barotropic plaitpoint occurs, which in connection with Comm. N⁰. 96*b* p. 12 pointed to the fact that for the knowledge of the course of the barotropic phenomena at lower temperature considerations in which only the transverse plait is taken into account, are not sufficient for these mixtures 3) (see Comm. N⁰. 96*c* p. 26).

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[1]) Considerations which are not in accord either with the limited compressibility of a gas at high pressures, first stated by NATTERER in 1844, or with our present views on the mixing of two substances, induced JAMIN, C.R. 96 (1883) p. 1448, Journ. de phys. (2) 2 (1883) p. 389 to raise the question whether it should be possible that with compression of a mixture of $CO_2$ with air or with hydrogen, a liquid phase would collect above the gas phase CAILLETET (JAMIN l.c., cf. CAILLETET and COLARDEAU, Journ. de phys. (2) 8 (1889) p. 392) did not succeed in realizing this.

In Comm. N⁰. 96*c* p. 23 footnote 1 an estimation 4) was

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1) On the peculiar phenomena which are met with in case of a barotropic plaitpoint, we hope shortly to make a communication.

2) That the barotropic plaitpoint found in Comm. N⁰. 96*c* § 5 belongs to the gas-liquidplait (cf. Comm. N⁰. 96*c* p. 22 footnote 1) was derived from the shape of the spinodal curve for this case, in connection with the course of the plaitpoint curve. The same thing may appear as follows: By applying the criterion (3) in Suppl. N⁰. 15, p. 15, we find that mixtures of a pair of substances with ratios indicated in the mentioned § belong to case (*c*) (cf. p. 6), while we may derive from van Laar's fig. 22, Arch. Teyler (2) 10 (1907) p. 138, Proc Kon. Akad. van Wet. Amst. Sept. '06, p. 226, fig. 1 that the plaitpoint curve crosses from the side $x = 0$ to the side $v = b$ (van Laar's type I).

3) For mixtures of pairs of substances as meant in Comm. N°. 96*c* table I p. 24 for which $0.219 > T_{k_2}/T_{k_1} > 0.196$, three barotropic plaitpoints will occur, one of which, however, does not belong to the absolutely stable region. At least for the larger ones of the mentioned ratios $T_{k_2}/T_{k_1}$, the two others belong to a plait which enters the $\psi$-surface from $K_1$, and crosses the $\psi$-surface as a transverse plait at lower temperature. For this the considerations of Comm. N⁰. 96*b* will hold, at least in so far as solid phases do not cause a disturbance. For the smaller ones of these ratios one of these two barotropic plaitpoints will also fall in the not absolutely stable fluid region, and so also for these we shall have to take the occurrence of three phase equilibria into account.

4) For the calculations in note 1, p. 23 of Comm. N⁰. 96*c* we availed ourselves for $a$ and $b$ of hydrogen of the values calculated for this by Kohnstamm (Landolt-Börnstein-Meyerhoffer's Physik. Chem. Tabellen 1905), which values had $T_k = 38.6$, $p_k = 20$ according to Olszewski, Wied. Ann. Bd. 56, p. 133, 1895 as starting point. If we derive the $a$ and $b$ for $H_2$ from $T_k = 29$ à 32, $p_k = 15$ according to Dewar (B. A. Report 1902), the estimation for $T_{k\mathrm{He}}$ yields about 1°; Olszewski's newer data, Ann. d. Phys. 17 (1905) p. 986: $T_k = 32.3$, $p_k = 14.2$, which yield $a_M = 0.000416$, $b_M = 0.001041$, give it a value of more than 1° (the calculation according to note 2 l.c. yields $a_{22M}/a_{11M} = {}^1/_{50}$, $T_{k\mathrm{He}} = 1.3$).

This would bring about these modifications in the classification of the derived about the critical temperature of helium from the observation of the barotropic phenomenon for a mixture of helium and hydrogen described in Comm. N°. 96*a* Nov. '06. In this estimation the supposition already mentioned in Comm. N°. 96*a*, p. 5, that the molecules of helium exert only an exceedingly slight mutual attraction was found confirmed.

This suggested the investigation already announced in Comm. N°. 96*b*, p. 10 on binary mixtures one of whose components is a gas, the molecules of which exert no or only feeble attraction (Suppl. N°. 15, Febr. '07). Here a plait was described for the first time which at descending temperature appears on the $\psi$-surface from the side of the small volumes, reaches the side $x = 0$ at $T = T_{k_1}$, and then passes into a plait crossing in a slanting

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helium mixtures mentioned in Suppl. N°. 15, § 8, that mixtures of He with $H_2O$, $O_2$, A, Ne, NO, $NH_3$ would belong to case (*b*), those with $H_2$, $H_2S$, $CO_2$ to case (*c*). For the modification which another assumption about $a_{12M}$ (cf. p. 11) would cause in the circumstances under which the plait starting from $v = b$ occurs see Suppl. N°. 15 p. 21. A smaller $a_{12M}$ might even again bring about a shifting in the classification in the direction from (*c*) towards (*a*).

For a newer estimation of the critical temperature of helium based on the determination of its isothermals see Comm. No. 102 *a* § 5. If that estimation will be verified by determinations at lower temparatures, an investigation about the properties of mixtures with $a_{12M}$ small compared with $\sqrt{a_{11M}\, a_{22M}}$ (cf. p. 11, for simplicity $a_{12M} = 0$ might be taken for a first investigation) or about the influence of the substances not following the equation of state mentioned Comm. No. 96 *c* § 3, with *a* and *b* not depending on *v* and *T* will prove desirable with reference to barotropic phenomena and phenomena of limited miscibility in the gas state for mixtures of helium. It is to be remarked here that the supposition $a_{12M}$ smaller with $a_{22M}$ less small according to Suppl. No. 15 § 1 furthers phenomena of limited miscibility, whereas the opposite influence of $a_{12M}$ becoming greater when $b_{He}$ for 20° and 40 atm. is larger than supposed Comm. No 96*b* p. 25 footnote 1—a supposition which also renders $T_{kHe}$ larger, whereas $b_{H_2}$ for 20°, 40 atm. considerably larger than $b_{H_2}$ for 32°, 14 atm., what would do the same, is not to be expected — is reduced by the fact that a larger $b_{He}$ considerably retards complete miscibility (cf. Suppl No 15 table I). So the general conclusions of Suppl No. 15 about limited miscibility retain their importance as possibly bearing on mixtures of helium as long as the experimental data on which the estimation of the critical temperature of helium is based remain unimpaired.

direction from $v = b$ to $x = 0$ [1]). This description was accompanied by remarks about limited miscibility in the gas state.

In Suppl. N⁰. 15 § 7, March '07, three cases were distinguished for mixtures in which one component is a gas with a feeble attraction. They are indicated as cases ($a$), ($b$) and ($c$) in § 9, May '07. Case ($a$) corresponds with the above mentioned one; in case ($b$) a plait coming from $v = b$ and one coming from $x = 0$ join to a single plait in a double plaitpoint [2]); in case ($c$) a plait starts from $x = 0$, comes in contact with $v = b$ at lower temperature, and passes then into a plait crossing in a slanting direction [3]).

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[1]) Cf. Suppl. N⁰. 15 p. 6 footnote 1.

[2]) On the suppositions mentioned in Comm. N⁰. 96$c$ p. 21 the data for the two double points in the net of spinodal curves of which this double plaitpoint is one (a node, cf. Suppl. N⁰. 15 p. 15) may be found in the following way (cf. Suppl. N⁰. 15, p. 19, note 5):

The equation for the $v,x$-projection of the spinodal curve on the molecular $\psi$-surface:

$$RTv_M{}^3 = 2(1-x_M)\,(v_M\sqrt{a_{11M}} - b_{11M}\sqrt{a_M})^2 + 2x_M(v_M\sqrt{a_{22M}} - b_{22M}\sqrt{a_M})^2 \quad (1)$$

(cf. Suppl. N⁰. 15 p. 5) gives, after some obvious reductions, as conditions for the appearance of a double point:

$$(v_M\sqrt{a_{11M}} - b_{11M}\sqrt{a_M})^2 = 2b_{11M}\sqrt{a_{11M}}.\,(1-x_M)\,(v_M\sqrt{a_{11M}} - b_{11M}\sqrt{a_M}) + \\ + 2b_{22M}\sqrt{a_{11M}}.\,x_M\,(v_M\sqrt{a_{22M}} - b_{22M}\sqrt{a_M}) \quad . \quad . \quad . \quad (2)$$

and

$$(v_M\sqrt{a_{22M}} - b_{22M}\sqrt{a_M})^2 = 2b_{11M}\sqrt{a_{22M}}.\,(1-x_M)\,(v_M\sqrt{a_{11M}} - b_{11M}\sqrt{a_M}) + \\ + 2b_{22M}\sqrt{a_{22M}}.\,x_M\,(v_M\sqrt{a_{22M}} - b_{22M}\sqrt{a_M}) \quad . \quad . \quad (3)$$

From (2) and (3) follows:

$$\frac{(v_M\sqrt{a_{11M}} - b_{11M}\sqrt{a_M})^2}{\sqrt{a_{11M}}} = \frac{(v_M\sqrt{a_{22M}} - b_{22M}\sqrt{a_M})^2}{\sqrt{a_{22M}}} \quad . \quad . \quad (4)$$

Extracting the root from this equation, we may reduce (2) and (3) to:

$$\frac{v_M\sqrt{a_{11M}} - b_{11M}\sqrt{a_M}}{\sqrt{a_{11M}}} = 2b_{11M}\,(1-x_M) \pm 2b_{22M}\,x_M\sqrt[4]{a_{22M}/a_{11M}} \quad . \quad . \quad (5)$$

and

$$\frac{v_M\sqrt{a_{22M}} - b_{22M}\sqrt{a_M}}{\sqrt{a_{22M}}} = 2b_{22M}x_M \pm 2b_{11M}(1-x_M)\sqrt[4]{a_{11M}/a_{22M}} \quad . \quad . \quad (6)$$

By eliminating $v_M$ from (5) and (6) we obtain for $x_M$ the equation (1) of Suppl. N⁰. 15 p. 15.

The further derivation of $v_M$ and $T$ (see Suppl. N⁰. 15 p. 18) may be left to the reader (compare with these developments VAN LAAR, Proc. Kon. Akad. Amst. May '07, p. 38 sqq. and Arch. TEYLER (2) 11 (1907) 1<sup>re</sup> partie § 5).

[3]) KUNDT, Berl. Sitzb. Oct. 1880, p. 812—824 was of opinion that it

For this distinction $a_{22M}/a_{11M}$ was always supposed so small in connection with the value of $b_{22M}/b_{11M}$, that the plaitpoint curve crosses from $K_1$ to the line $v = b$ and that three phase equilibria not yet occur at the temperatures under consideration ¹).

Now that the estimations concerning the $a$ and $b$ of helium

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would always be possible to convert a liquid to the gas state by pressing in a gas. This view was maintained in van Eldik's thesis (Leiden 1898, p. 7, cf. Suppl. N°. 3, p. 45), where it says that the operation mentioned, if it is realized, would be the determination of the plaitpoint pressure corresponding to the temperature of observation of the pair of substances which is subjected to the experiment. There it was tacitly assumed, that with sufficiently high pressure the plaitpoint state could be reached for every temperature between the critical temperatures of the components as e.g. for mixtures of methyl chloride and carbonic acid, even though it would have to be found above 750 atmospheres for hydrogen and ether, as van Eldik derived taking into account the diminution which with increasing pressure is found in the decrease of the surface tension caused by one and the same increase of pressure (Kundt loc. cit. p. 818; van Eldik Thesis, p. 5, cf. Suppl. N°. 3, p. 52). If we pay attention to the possibility now foreseen by the theory, that this diminution continues outside the region of observation, it seems probable in the light of the observations mentioned, that it would not be possible — here we treat as infinite, pressures which exert forces on the molecules greater than those joining the parts of them — to reduce the surface tension to 0 for the pair of substances mentioned (and the same remark applies to hydrogen and ethylalcohol) at the temperature of observation (Kundt 21°, van Eldik 9°.5), so that already at that temperature a plait crossing obliquely from $x = 0$ to $v = b$ would exist on the $\psi$-surface.

In fact we should also derive from van Laar's figure cited p. 4 footnote 2 that ether-hydrogen (and also alcohol-hydrogen) belong to van Laar's type I, whereas according to the criteria laid down by us, they should belong to case (*c*) of this type. Van der Waals's equations Contin. II p. 43, however, would point out a critical temperature of complete miscibility of about −200°C. in the supposition of $a_{12M} = \sqrt{a_{11M}\, a_{22M}}$, so that according to these suppositions an obliquely crossing plait would only make its appearance below this temperature. If the existence of an obliquely crossing plait at the temperature of the above mentioned experiments should be confirmed, this might among other things point to the fact that $a_{12M}$ would be considerably smaller than $\sqrt{a_{11M}\, a_{22M}}$ for the pair of substances mentioned (cf p. 11).

¹) According to this restriction case (*c*) cannot occur e.g. for $b_{22M}/b_{11M}$ larger than a certain value (cf. Suppl. N°. 15 p. 16).

justify the supposition that the plaitpoint curve[1]) crosses from $x = 0$ to the line $v = b$ for mixtures of helium and hydrogen[2]), it is desirable to subject the barotropic phenomena for the cases mentioned to a closer examination. In this discussion for mixtures one component of which is a gas with feeble attraction, we shall again restrict ourselves and suppose that in the considered cases at the considered temperatures the second branch of the plaitpoint curve (VAN LAAR, Proc. Kon. Akad. Amst. May '05 p. 37), starting from $K_2$, does not make its influence felt, so that three phase equilibria do not yet make their appearance.

§ 2. *The course of the barotropic phenomena for binary mixtures, one component of which is a gas whose molecules exert only a feeble attraction.*

In this discussion we shall have to distinguish the cases (*a*), (*b*), and (*c*) mentioned in § 1.

*a.* In this case a plait starting from $v = b$ and closed towards the side of the large $v$'s, appears for $T_{km} > T > T_{k_1}$, which plait we have called gas-gasplait in Suppl. N⁰. 15 p. 11. If $b_{22} < b_{11}$, then $\theta_{pl}$ will be $> \frac{\pi}{2}$ for $T > T_{bpls}$ (see Comm. N⁰. 96*b* p. 12); at $T = T_{bpls}$ a barotropic plaitpoint occurs (cf. Suppl. N⁰. 15 Pl. I, fig 1); at $T < T_{bpls}$ we find a barotropic nodal line on the gas-gasplait (cf. Suppl. N⁰. 15, Pl. I, fig. 2). At $T = T_{k_1}$ the gas-gasplait passes into an obliquely crossing gas-liquidplait. A barotropic nodal line will exist on it (see fig. 1) till it disappears under the three phase triangle, and so passes into the not absolutely stable region. As mentioned in § 1 we shall not give the description of what happens when three phase equilibria have appeared. In the same way we shall for the present disregard more complicated cases, as the appearance of two barotropic nodal lines on the gas-gasplait, three on the obliquely crossing plait etc., till further investigation may teach that these cases are possible.

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[1]) KUENEN, Proc. Kon. Akad. Amst. Febr. '03, p. 473 was the first to find experimentally a plaitpoint curve starting from $x = 0$, and directed to the side $v = b$, for mixtures of ethane and methylalcohol.

[2]) This follows also from VAN LAAR's fig. 22, Arch. TEYLER (2) 10 (1907) p. 38 with the mentioned estimations on the critical temperature and pressure of helium (cf. p. 4 note 4) and on the suppositions made (cf. Comm N⁰. 96*c* p. 21).

If $b_{22} > b_{11}$, the plait coming from $v = b$ may reach the side $x = 0$, and pass into an oblique plait without it being necessary that a barotropic tangent chord occurs.

*b*. For $b_{22} < b_{11}$ a barotropic plaitpoint will occur at $T_{bpls} > T_{dpl}$ (cf. Suppl. N⁰. 15 p. 17). This barotropic plaitpoint, and also at $T_{bpls} > T > T_{dpl}$ the barotropic tangent chord, may occur either on the plait starting from $v = b$ or on that starting from $x = 0$ (figs. 2 and 3). If in the homogeneous double plaitpoint the isobar should run parallel to the $x$-axis, $T_{bpls}$ would coincide with $T_{dpl}$. For $T < T_{dpl}$ a barotropic chord exists on the obliquely crossing plait, just as in case (*a*) [1]).

For $b_{22} > b_{11}$, as in this case for (*a*), the existence of barotropic tangent chords is not required.

*c*. If $b_{22} < b_{11}$, a barotropic plaitpoint will make its appearance for $T_{bpls} < T_{k_1}$ and $> T_{km}$; at lower temperatures a barotropic tangent chord is found on the plait starting from $x = 0$ and closed on the side of the small $v$'s and at $T < T_{km}$ on the obliquely crossing plait (fig. 4). For $b_{22} > b_{11}$ as for (*a*) and (*b*).

In fig. 5 the course of the spinodal curves (continuous) and of the connodal curves (lines consisting of dashes) on the $\psi$-surface for the unit of weight has been more fully represented for a case (*c*). The figure has been constructed with a view to mixtures of helium and hydrogen. In this we adopted the hypotheses mentioned in Comm. N⁰. 96*c*, Dec. '06, p. 21, and put for hydrogen $T_{k_1} = 32.3$, $p_{k_1} = 14.2$, for helium $T_{k_2} = 1.3$, $b_{\mathrm{MHe}} =$

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[1]) In the light of our present knowledge of the behaviour of mixtures and divested of the considerations which are incompatible with it (cf. p. 3 footnote 1) the phenomenon deemed possible by Jamin, C. R. 96 (1883) p. 1451, Journ. de phys. (2) 2 (1883) p. 393, would be described as follows: On compression of a gas above a suitable quantity of liquid (see p. 12 note 2), this liquid is made to dissolve at first under plaitpoint circumstances after which on further pressing in of the gas into the thus formed homogeneous phase, a phase richer in the least volatile component (called by Jamin liquid, by us in certain cases, cf. Suppl. No. 15, § 4, second

$\frac{1}{2} b_{MH_2}$ (p. 4 note 4)[1]. The volume $v$ is expressed in the theoretical normal volume of a molecular quantity as unit. The point $K_m$ has been calculated according to VAN DER WAALS Cont. II, p. 43. The spinodal curves have been constructed as in Suppl. N$^0$. 15 § 2. $P_b$ is the barotropic plaitpoint, calculated in the way indicated in Comm. N$^0$. 96*c* § 4. Further the plaitpoint curve $K_1 K_m$ calculated according to the equation given by VAN LAAR, Proc. Kon. Akad. Amst. April '05 p. 652, has been included in the diagram. The second branch of the plaitpoint curve is not to be distinguished from the straight line $HK_2$ on the scale on which the diagram has been drawn.

For the connodal curves the points of intersection with the line $x = 0$ representing the points of saturation for pure hydrogen have been calculated. For this purpose the constants of saturation have been used, which have been calculated by DALTON [2]) for a substance that follows the equation of state of VAN DER WAALS with constant $a$ and $b$. For the rest the course of the connodal curves for which for $T \geqq T_{km}$ also the plaitpoints are known, has been represented schematically. This applies particularly to the points of intersection of the connodal curve for $T = 20$ with the line $v = b$, so that also the course of the connodal curve, particularly of the gas branch, is uncertain in the neighbourhood of the line $v = b$. The line $CD$ represents the experimentally determined barotropic tangent chord for $T = 20$ (see Comms. N$^0$. 96*a* and N$^0$. 96*c* p. 23 footnote 1).

The situation of the line $CD$ with respect to the connodal curves might point to $T_{km}$ being higher than was calculated by us, which may be due either to the critical temperature of helium being lower

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gas phase) may separate *above* the phase which is richer in the most volatile component. If this phenomenon could be realized, we should have to deal with a case (*b*) for a temperature $T > T_{dpl}$, and in which the line $BQ$ (see fig. 6) intersects the plait starting from $v = b$ in such a way that for the intersected connodal tangent chords $\theta > \frac{\pi}{2}$.

[1] However, on account of the uncertainty which still prevails about $T_{kHe}$ and $p_{kHe}$, and in view of the probability that $a_{12M} < \sqrt{a_{11M}\, a_{22M}}$ (see p. 11) it is still to be considered as quite possible that He — H$_2$ belongs to case (*b*), as was supposed in Suppl. N$^0$. 15.

[2] J. P. DALTON. Phil. Mag. April 1907, p. 520.

than was assumed by us here, or to $a_{12M}$ being $< \sqrt{a_{11M}\, a_{22M}}$ for mixtures of He — $H_2$ [1] [2].

The course of the barotropic plaitpoints and barotropic tangent chords in case (*c*), and also in case (*b*), if they occur on the plait starting from $x = 0$, corresponds for the higher temperatures with that for the case that the branch of the plaitpoint curve starting from $K_1$ crosses the $\psi$-surface from $x = 0$ to $x = 1$, for which case the course was described in Comm. N⁰. 96*b*. For the lower temperatures we meet with this difference that in the cases considered in this Comm. the barotropic tangent chord continues to exist on the plait, till it disappears under the three phase triangle, whereas in the cases considered in Comm. N⁰. 96*b* the barotropic tangent chord may also vanish from the plait through a barotropic plaitpoint (lower barotropic plaitpoint temperature, see Comm. N⁰. 96*b* p. 12). The latter must even be the case if for $T \geqq T_{k2}$ no three phase equilibria appear as yet (cf. p. 4 note 3).

Van der Waals, Proc. Kon. Akad. Amst. Jan. '07 p. 528 calls attention to the influence of $b_{22}/b_{11}$ on the occurrence of barotropic phenomena by stating this rule: "When the most volatile substance has the greatest limiting density, the gas phase can be specifically heavier than the liquid phase." In connection with what was discussed above we may now supplement this rule as follows: If of a binary mixture the more volatile component has the greater limiting density, the gas phase will be made to sink in the liquid phase by compression with suitable concentration and temperature, provided the more volatile component has so feeble an attraction that pressing in of this latter component cannot make the liquid phase of the less volatile component dissolve in the gas phase at definite [1]) temperatures even at the highest (comp. p. 6 note 3) pressures [2]). It is implied in the terms of this rule that it has been supposed that no two liquid phases occur.

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[1] The same remark concerning $a_{12M}$ for mixtures of $H_2$ with other substances might be derived as follows: for $CO_2$ -- $H_2$ (the same holds for $CO_2$ –$O_2$) from a comparison of the experimentally determined portion of the plaitpoint curve with that calculated in the same way as above for He—$H_2$ (cf. Suppl. No. 19, errata and addenda to Suppl. No. 11); for $H_2$ — ether and $H_2$ — alcohol see § 1 p. 6 note 3).

[2] The deviating of the substances mentioned, in particular of $H_2$, from Van der Waals's equation of state with constant *a* and *b*, may have a same influence on the position of the barotropic tangentchord.

It is not excluded that also in other cases sinking of the gas phase in the liquid phase might occur [3]).

If we apply this rule to pairs of substances of which data are availabe for $a_{22M}$, $a_{11M}$ and $b_{22M}$, $b_{11M}$, it appears that only for $He-H_2$ it may be expected on reasonable grounds [4]) that barotropic phenomena occur at not too high pressures [5]). Further investigations will have to reveal whether for mixtures of pairs of substances as nitrogen and a light oil with high critical temperature [6]), nitrogenlithium, argon-kalium, mercury-iron etc. sinking of the gas phase in the liquid phase can be realized.

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[1]) Also at higher temperatures than these barotropic phenomena may then occur.

[2]) In the case of compression of a gas above a liquid, starting from the pure substance in the way as was done in KUNDT's experiments we describe on the $\psi$-surface a curve the $v, x$-projection of which is a straight line joining a point of the line $x = 0$ with the point $v = 0$, $x = 1$. Indeed, if $m_1$ is the mass of the first component, occupying the volume $V$ (which we think constant), and $m_2$ the mass of the second component pressed into that volume, we derive from $x = \frac{m_2}{m_1 + m_2}$ and $v = \frac{V}{m_1 + m_2}$ for the $v$, $x$-projection of the curve described: $m_1 \; v = V \; (1-x)$. For the liquid phase to disappear at a definite, suitable temperature just under plaitpoint circumstances $P$ (in fig. 6), we must start from a definite quantity of liquid so that the volume is represented by $SQ$ (see fig. 6). If the quantity of liquid from which we start, is smaller, the liquid phase will evaporate (be dissolved in the gas phase), if it is larger the gas is dissolved in the liquid phase (cf. VAN DER WAALS, Cont. II, p. 136). Only if the diffusion is not rapid enough to ensure equilibrium all through the tube, solution of the liquid under plaitpoint phenomena may be observed also with other quantities of liquid as corresponding with $v_Q$, as has been set forth by KUENEN's experiments on the influence of phenomena of retardation.

[3]) See e.g § 1, p. 4 note 3.

[4]) Though for mixtures of e.g. helium and acetonitril the available data with application of the special hypotheses assumed in this § (concerning the equation of state etc), would point to the fact that at high pressures barotropic phenomena might still just occur, it is impossible to express a definite expectation with regard to this on account of the influence of the uncertainties, both in the data and in the validity of the mentioned suppositions.

[5]) This was mentioned in Comm. N°. 96*b* p. 13.

[6]) Mr. F. M. GILLEY of Boston drew our attention to mixtures of air and oil.

§ 3. *On the conditions for the occurrence of barotropic phenomena.*

It appeared in § 2 that with a suitable ratio of the limiting densities the occurrence of the barotropic phenomena depends to a great extent on the ratio of the attractions of the molecules of the two components, hence on the ratio of the critical temperatures. The same thing may also be derived in the following way, more independent of the particular hypotheses which have led to the consideration of obliquely crossing plaits.

To bring about the phenomenon of the gas phase sinking in the liquid phase, the gas phase will have to be much more compressible than the liquid phase, and even on compression the gas phase must not dissolve in the liquid phase. For this the temperature will have to be pretty far below the critical temperature of the least volatile component ($T_{k1}$), but still far above that of the second component ($T_{k2}$). This points to a large difference between the critical temperatures of the components.

If for the pair of substances considered retrograde condensation of the first kind occurs, the coexisting phases indicated by the points $L$ and $G$ on the $\psi$-surface for the molecular quantity (see fig. 7) [1]), can only have the same density if $M_2 > M_1$.

Only when on the plait on the molecular $\psi$-surface connodal taugent chords appear for which the angle with the axis $x = 0$: $\theta > \frac{\pi}{2}$, the coexisting phases can have equal density for $M_2 < M_1$.

As the difference between $x_g$ and $x_l$ is larger, and so the connodal tangent chords deflect more rapidly from the side $x = 0$, a smaller difference between $M_2$ and $M_1$ will suffice to establish equal densities in $G$ and $L$.

This will be the more the case the more the plait extends towards the side $v = b$.

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[1]) The dotted lines in that figure indicate that the considerations of this § hold both for the case that at lower temperature the plait crosses the $\psi$-surface as a transverse plait, and for the case that it extends towards $v = b$ as an obliquely crossing plait.

The latter is particularly furthered by a small ratio $a_{22M}/a_{11M}$ (cf. Suppl. N⁰. 15 Pl. I fig. 1 and Pl. II), so by a small ratio of the critical temperatures, $b_{22M}$ smaller than $b_{11M}$ also tending in this direction.

Hence we get as conditions for the possibility of the occurrence of barotropic phenomena:

The second component must have: $T_{k_2}$ small compared with $T_{k_1}$, and by preference also: $M_2 > M_1$ and $b_{22M} < b_{11M}$.

This becomes still clearer by the application of equations (2) and (4) of Comm. N⁰. 79, March '02:

$$x_l = x_g e^{\frac{\Phi'_g - \Phi'_l}{MRT}}$$

$$\frac{\Phi'_g - \Phi'_l}{MRT} = \left\{ \alpha \frac{T}{p_m} \frac{dp_m}{dT} - \beta \right\} \frac{p_m (v_g - v_l)}{MRT}$$

which determine the ratio of the concentrations of gas and liquid phases of a binary mixture in which the quantity of one component is small, if the law of the corresponding states may be applied. The connodal tangent chord will rapidly deflect from the side $x = 0$, if the exponent of $e$ assumes a considerable negative value. The greatest influence on this exerts $\alpha = \frac{1}{T_{k1}} \left( \frac{d T_{xk}}{dx} \right)_{x=0}$, on account of the value of the coefficient $\frac{T}{p_m} \frac{dp_m}{dT}$ $(> 7)$; so $T_{k_2}$ will have to be small with respect to $T_{k1}$. The influence of $\beta = \alpha - \gamma$, if $\gamma = \frac{1}{v_{k1}} \frac{dv_{xk}}{dx}$ (cf. Comm N⁰. 81 p. 8) is only of secondary importance. To tend at least in the right direction, $\gamma$ would have to be negative, so $b_{22M} < b_{11M}$ [1]).

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[1]) The more elaborate mathematical treatment of the conditions for the occurrence of barotropic phenomena, as sequel to Comm. No. 96c, will be postponed till further experiments call for a further discussion.

[illegible]

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

## Supplement No. 17
## to N°. 97—108.

**Dr. H. KAMERLINGH ONNES and J. CLAY.** "Some remarks on the expansion of platinum at low temperatures".

(*Translated from: Verslagen van de Afdeeling Natuurkunde der Kon. Akademie van Wetenschappen te Amsterdam,* **28 September 1907**, p. 243—245).

EDUARD IJDO — PRINTER — LEIDEN.

**Dr. H. KAMERLINGH ONNES and J. CLAY.** "*Some remarks on the expansion of platinum at low temperatures*".

The communication from the "Physikalisch-technische Reichsanstalt" by K. SCHEEL in the meeting of Jan. 11, 1907 of the "Deutsche physikalische Gesellschaft" led us to make a remark already in the Meeting of June 29, 1907. In Communication N$^0$. 95*b* (June '06) we had given a quadratic formula for the expansion of platinum *below* 0°, from which followed that, as was remarked in the introduction of that Communication, a formula of the third degree is required if we wish to represent the expansion of platinum from — 180° to + 100° by one polynomial with increasing powers of $t$, and if we have to deal with observations which if repeated a sufficient number of times, allow us to reach an accuracy (comp. § 1 of Comm. N$^0$. 85, June '03) of $^1/_{200}$ in the expansion. We found this confirmed by the measurements of SCHEEL, who arrived at the same result by determining a quadratic formula for the expansion of platinum *above* 0°, and by measuring the length at — 190°.

We now consider the striking difference of the expansion at low temperatures according to the formula given by us, and that according to SCHEEL's formula, viz: 43 $\mu$ for the expansion for a bar of 1 meter between — 183° and + 16° (cf. SCHEEL loc. cit. p. 19, note 1), a difference much greater than could be accounted for by the inaccuracy of the observations.

For an explanation of this discrepancy we call attention to the difference of the observations of Dec. 16, 1904 and Febr. 3, 1905 in Table II of Comm. N$^0$. 95*b*, which give as length of the platinum bar provided with the two glass extremities, at 16° [1]) before it had ever been reduced to low temperature, 1027.460 m.m., and a long time after it had been reduced to low temperature for the last time, 1027.457 m.m., mean 1027.458 m.m., with those of Dec. 19, 21 and 23 in the same table which yield the mean value 1027.441 m.m. (from 1027.441, 1027.442 and 1027.440) for the length at 16°, which was observed on return to the ordinary temperature a day after the cooling. Indeed this former mean value is 17 $\mu$ larger than the latter.

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[1]) In Table II of that communication under $L_{16°}$ for the ordinary temperatures the length of the bar at 16° reduced on the measuring rod *at 16°* has been given and not the length at $\vartheta$ as in the tables of Comm. N°. 85.

Now this difference of 17 $\mu$, which refers to a bar of platinum of 840 mm. (for a bar of 1 M. it would be 20 $\mu$) exceeds the errors which may be ascribed to the inaccuracy of the observation by about half the difference which exists between Scheel's formula and our formula of June 1906.

As basis for the calculation of our formula the mean [1] of the two lengths has been taken. We arrive at values for the expansion nearer to those of Scheel when for the length at the ordinary temperature we take that which was found immediately after cooling, instead of the mean of this length and the length which was found long before and after the cooling, as was done in the calculation of our formula of June 1907. If we now make use of the firstmentioned length, that which was found immediately after cooling, in order to find the coefficients now distinguished by $(a)$ and $(b)$ from the former $a$ and $b$ in the formula:

$$l_t = l_0 \left[ 1 + \left\{ (a)\left(\frac{t}{100}\right) + (b)\left(\frac{t}{100}\right)^2 \right\} 10^{-6} \right]$$

we find:

$$\begin{array}{c}\textbf{Platinum}\\ (-183^\circ \text{ to } +16^\circ)\end{array} \left\{ \begin{array}{l} \left.\begin{array}{l}\text{(a) } 877.7\\ \text{(b) } \;\;35.7\end{array}\right\} \begin{array}{l}\text{Kamerlingh Onnes}\\ \text{and Clay (1905)}\end{array} \\ \qquad\qquad\qquad \text{whereas} \\ \left.\begin{array}{l}\text{(a) } 861.5\\ \text{(b) } \;\;37.0\end{array}\right\} \text{Scheel (1906)} \end{array}\right.$$

It is true that the now remaining difference of 34 $\mu$ per M. with an expansion of — 188° to + 16° remains considerably larger than the accuracy of the observations would lead us to expect, but it is considerably smaller than that found originally, and taking into consideration the different sources of uncertainty whether we observe really what we think we observe, the small number of measurements, and the difference of the methods applied at low temperatures for the first time, it is not great.

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[1] In the calculations for the glass the values of the length immediately after the cooling, Dec. 23 in Table I, and April 15 and 16 in Table III, have been left out of account in connection with the further observations.

We had hoped to obtain further information on the difference in length of our bar at ordinary temperature immediately after the cooling and long after it, but have not yet been able to do so.

Differences as the one discussed now have more occurred in our measurements. We have pointed this out in Comm. N$^0$. 95*b* and for glass we there have expressly investigated the possibility of thermical hysteresis on cooling to the lowest temperatures. In connection with what has been said in Comm N$^0$. 95*b* we fear that for the above treated difference an irregularity in the behaviour of the place of fusion of the glass points to the platinum bar has played a part, to prevent which further experiments ought to be made with still greater care. If what we now think probable, is verified, observations in which a difference as the one considered just now, manifests itself, should be rejected.

Besides the formula of the second degree for temperatures below 0°, we have also calculated a formula of the third degree

$$l_t = l_0 \left[ 1 + \left\{ (a') \frac{t}{100} + (b') \left(\frac{t}{100}\right)^2 + (c') \left(\frac{t}{100}\right)^3 \right\} 10^{-6} \right]$$

for the expansion of platinum between — 183° and + 80° by the aid of Benoit's observations from 0° to + 80°, in which formula $(a')$ $(b')$, $(c')$ refer to the length at the ordinary temperature immediately after the cooling.

The agreement of

| | | | | |
|---|---|---|---|---|
| Platinum | + 80° | (a′) | 875.3 | Benoit and Kamerlingh Onnes and Clay (1905) |
| | to | (b′) | 31.6 | |
| | — 183° | (c′) | —1.49 | |
| | + 100° | (a′) | 874.9 | Scheel (1906) |
| | to | (b′) | 31.41 | |
| | — 190° | (c′) | —6.94 | |

is pretty satisfactory. Substitution of Scheel's values for those of Benoit would bring about only a slight change in the first group of coefficients.

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*Director of the Laboratory.*

## Supplement No. 18*a*

## to No. 97—108.

**Dr. H. KAMERLINGH ONNES.** “Die Cascade zur Erhaltung tiefer Temperaturen bis —259° C.”

(*Translated from: Handelingen van het* 11$^{\text{de}}$ *Nederlandsch Natuur- en Geneeskundig Congres te Leiden*, **5 April, 1907**, p. 164—169).

EDUARD IJDO — PRINTER — LEIDEN.

## **Dr. H. KAMERLINGH ONNES.** *Die Cascade zur Erhaltung tiefer Temperaturen bis* —259° C. [1]

Die Demonstration im physikalischen Institut hatte den Zweck verschiedenes zu zeigen, das sich bezieht auf das Arbeiten mit flüssigem Wasserstoff, und auf die Untersuchung der physikalischen Eigenschaften der einatomigen Stoffe, unter denen das Helium wieder die bedeutendste Stelle einnimmt. Wie gerne der Redner auch weiter ausgeführt hätte über die Bedeutung und den Zweck genauer Messungen bei tieferen Temperaturen [2], über allerhand thermische, optische, elektrische und magnetische Eigenschaften, meinte er jetzt den Wünschen der Besucher besser zu entsprechen indem er ihnen so viel wie möglich Gelegenheit gäbe sich durch eigene Anschauung ein Bild zu schaffen von der Eigentümlichkeit der Untersuchung auf dem Gebiete tiefer Temperaturen, besonders bei den ausserordentlich tiefen Temperaturen, welche man mittelst flüssigen Wasserstoffes bekommen kann.

Er beschränkte sich also auf die Mitteilung einiger Gegenstände, bei denen die absolute Temperatur eine wichtige Rolle spielt — die thermodynamische Zustandsgleichung, besonders jene von Helium und Wasserstoff, die magnetische Drehung der Polarisationsebene in Wasserstoff und Helium, den galvanischen Widerstand reiner Metalle — um das zu demonstrirende Gebiet der Untersuchung, besonders das der äusserst tiefen Wasserstofftemperaturen zu charakterisiren als gehörend zu jenem Abschnitt der Physik, welchen man die Physik der Atomen zu nennen anfängt, und den das zwanzigste Jahrhundert so ganz anders zur Hand nimmt wie das neunzehnte.

Der Redner verweilte erstens bei der Weise in welcher man constante gleichmässige, tiefe Temperaturen herstellt. In Leiden be-kommt man diese indem man flüssige Gase bei normalem oder vermindertem Druck verdampfen lässt. Die Apparate, in welchen das verflüssigte Gas auf gleichmässiger, constanter Temperatur gehalten wird, wurden von Fräulein JOLLES demonstrirt. Einen Augenblick verweilte der Redner bei den Hülfsmitteln, welche in Leyden so reichlich über die verflüssigten Gase verfügen lassen, wie es für viele dort angestellten Untersuchungen notwendig ist. Die für diesen Zweck eingerichtete Cascade von Gascirculationen, durch welche der Redner im Stande ist sogar bei —259° noch über ein Flüssigkeitsbad von einigen Litern zu verfügen, das bis auf $^1/_{100}$ Grad konstant bleibt so lange man es wünscht, wird vom Redner beschrieben mit Hilfe einer Zeichnung [1]), die im eigentlichen kryogenen Laboratorium auch aufgehängt ist, und worauf die verschiedenen Cirkulationen mit denselben Farben angegeben sind, wie die Apparate im Laboratorium gemalt sind, während zur weiteren Wiedererkennung auf den Apparaten dieselben Buchstaben und Zahlen angebracht sind wie auf der Zeichnung. Eine derartige Anweisung war wegen der grossen Anzahl der Besucher notwendig. Das kryogene Laboratorium macht, wegen der grossen Anzahl Details und Hilfsapparate für spezielle Zwecke beim ersten Anblick einen verwirrenden Eindruck; jene Details und Hilfsmittel können für eine Demonstration nicht abgebrochen werden; ausserdem sind sie gerade charakteristisch für die wissenschaftliche Arbeit, für welche die Cascade dient.

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[1] Vortrag und Demonstration gehalten im physikalischen Institut vor der Abteilung Physik des 11ten Congresses Niederländischer Naturforscher und Aerzte zu Leiden, 5 April 1907.

[2] H. Kamerlingh Onnes. Die Bedeutung genauer Messungen bei sehr tiefen Temperaturen. Comm. Suppl. No. 9, 1904.

Die Beschreibung der drei ersten Cirkulationen der Cascade, Chlormethyl, Aethylen, und Sauerstoff, veranlasste den Redner über die Zufügung der Regeneratoren zu sprechen, durch welche die Leidener Methode vom Anfang an sich auch prinzipiell unterschieden hat von der PICTET'schen Cascademethode, und welche für das Wohlgelingen der Arbeit von grosser Bedeutung gewesen ist. Weiter erwähnt er, dass neben der Anwendung der Cascade von Cirkulationen um auf immer tiefere Temperaturen hinabzusteigen, jede Cirkulation Gelegenheit giebt, das flüssige Gas auch in einen anderen Apparat, als den Refrigerator jener Cirkulation abzuschenken, zum Beispiele in einen Kryostat, und das verdampfte Gas aus demselben hinwegzusaugen um es wieder als Flüssigkeit zur Verfügung zu stellen, und mit einer und derselben geringen Quantität Flüssigkeit die gewünschte Temperatur in den Apparaten so lange zu unterhalten wie man es wünscht. Mit Chlormethyl umspannt man von —23° bis —90°, mit Aethylen von —103° bis —165°, mit Sauerstoff von —183° bis —217°.

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[1]) Ähnlich der bei MATHIAS, Le laboratoire cryogène de Leyde, Rev. Gén. des Sc. 30 Avr. 1896, für die damaligen drei ersten Cyclen.

Die vierte Cirkulation liefert flüssige Luft. Ein Kompressor saugt die gewöhnliche atmosphärische Luft an und verflüssigt dieselbe in der Kühlschlange mit Regenerator, welche im flüssigen Sauerstoff getaucht ist. Während die früheren Cirkulationen geschlossen waren, weil die reinen Gase, welche sie enthalten, nicht verloren gehen und mit Luft vermischt werden dürfen, braucht dies bei der Luftcirkulation nicht der Fall zu sein. Die Vorteile welche sich daraus ziehen lassen, dass man flüssige Luft in Vakuumgläser sammeln und aufbewahren kann, um dieselbe an irgend einem andern Ort, oder später verdampfen zu lassen, sind augenfällig. Mehrere Liter in Leiden aufgefangene, flüssige Luft sind weit über der Grenze, bis in Strassburg und Eger in Böhmen [1]) verdampft. Ein permanenter Vorrat von einigen Zehnern Litern wird in Leiden fortwährend unterhalten, und zu wiederholten Malen hatte der Redner das Vorrecht damit Physikern und Chemikern nach Anfrage dienlich zu sein, was jetzt noch leichter geworden ist, nun in Folge der Bemühungen des Redners, die Versendung per Eisenbahn zugestanden ist. Die Cirkulation erlaubt leicht mehr als ein halbes Hektoliter flüssige Luft pro Tag zu erhalten; dies geschah u. a. noch gestern behufs dieser Demonstration. Es ist auch wünschenswert über ein so grosses Vermögen zu verfügen um mit einer Wasserstoffcirculation, wie diese für die Leidener Messungen notwendig ist, leicht arbeiten zu können.

Bei der Beschreibung der Wasserstoffcirkulation lenkt der Redner die Aufmerksamkeit auf das Charakteristische davon, nämlich, dass sie für continuirliche Arbeit eingerichtet ist. Sie ist deshalb mit der grössten Sorgfalt geschlossen und der cirkulirende Wasserstoff ist mit besonderer Sorgfalt gereinigt. 5 M$^3$. Wasserstoff werden vier Mal pro Stunde rundgeführt und schon wenige Kubikmillimeter feste Luft reichen hin um die feinen Kanäle, durch welche der Wasserstoff sich bewegen muss, zu verstopfen.

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[1]) Nachher noch in Paris.

Deshalb kommt es bei allen Versuchen darauf an, den reinen Wasserstoff zu bewahren. Versuche, wie bei der gemachten Demonstration, — behufs welcher mehr als zehn Liter flüssigen Wasserstoff bereitet war, — würden bei der täglichen Arbeit wie eine Verschwendung betrachtet worden sein [1]).

Der Redner zeigte alsdann den flüssigen Wasserstoff in einem Vakuumglase, umhüllt von einem Vakuumglase mit flüssiger Luft. Um zu beweisen dass der Siedepunkt bei etwa 21° absolut liegt, wurde ein kleines Thermometer- oder Piezometergefäss hineingetaucht, das mittelst eines umgebogenen Rohres in Verbindung steht mit einer Kugel von nahezu dreizehn- und daunten mit einer zweiten von nahezu vierzehnmaligem Volumen, an dessen Ende der eine Schenkel eines Manometers anfängt der mit dem andern Schenkel mittelst eines Kautschukschlauches verbunden ist. Dieser Apparat ist mit soviel Helium gefüllt worden, dass es bei Zimmertemperatur nahezu Barometerdruck zeigt. Beim Eintauchen des Gefässes in den flüssigen Wasserstoff füllt das Quecksilber die erste Kugel. Dass das Gas im Thermometer Helium ist, wird demonstrirt dadurch, dass man auch die zweite Kugel mit Quecksilber füllt, wofür der Druck verdoppelt werden muss. Dieser Versuch ist geeignet um zu zeigen dass komprimirtes Helium bei der Temperatur des flüssigen Wasserstoffs eine bedeutende Dichtigkeit erlangt. Diese grosse Dichtigkeit spielt eine Rolle beim Sinken von Gas in Flüssigkeit (vergl. Comm. N°. 96*a* und die Demonstration von Dr. KEESOM, Suppl. N°. 18*b*.) Es ist weiter einleuchtend dass das Piezometer, zur Bestimmung der Isothermen von Helium beim Siedepunkt und Gefrierpunkt des Wasserstoffs, von grossen Dimensionen sein muss, wenn einigermassen genaue Resultaten in Betreff des kritischen Zustandes von Helium daraus gefolgert werden sollen (die Piezometer wurden demonstrirt von Herrn BRAAK). Die Kenntniss dieser kritischen Daten ist von grosser Bedeutung; sie wird der Verflüssigung von Helium vorangehen müssen, wie die Berechnung der kritischen Daten des Sauerstoffs der Verflüssigung dieses unter den permanenten Gasen zuerst verflüssigten Gases voranging.

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[1]) Ein Apparat, um mittelst des cirkulirenden reinen Wasserstoffs, leicht weniger reinen für Versuche zu verflüssigen, ist in Bearbeitung. (In 1907 wurde noch ein Apparat zur Reinigung von gasförmigem Wasserstoff mit Hülfe von flüssigem Wasserstoff fertig gestellt).

So viel steht schon fest, dass die kritische Temperatur von Helium nicht mittelst Verdampfung des Wasserstoffs wird erreicht werden können. Schätzungen in Betreff der kritischen Daten von Helium, worüber Dr. Keesom handeln wird, machen es wahrscheinlich dass man sich auch den Joule-Kelvin-effect nicht zu Nutzen machen können wird, um das Helium zu verflüssigen [1]). Dies letztere wird also sehr schwer sein. Täuscht das uns in unserem Wunsche das Helium bald flüssig zu sehen, wir müssen uns deshalb erfreuen, dass die Temperatur bei welcher Helium in derselben Weise wie die andren Gase verflüssigt werden kann nicht so leicht erreichbar ist, denn es wird dadurch möglich sein einzudringen in ein Gebiet von Temperaturen, das besonders für die Lehre der Elektronen vielversprechend ist, und das, wenn das Helium leicht verflüssigte, auf immer verschlossen scheinen würde, bis etwas ganz Unerwartetes entdeckt werden sollte.

Der Redner behandelte weiter den Gebrauch des Wasserstoffs zur Erhaltung hoher Vakua. Mit einem mit Sauerstoff gefüllten Entladungsrohr, von welchem ein Seitenrohr in flüssigen Wasserstoff getaucht werden kann [2]), zeigt er, wie vollständig und augenblicklich man das Vakuum bis zu jedem gewünschten Druck einstellen kann, was für das Studium der Entladungserscheinungen von höchster Bedeutung ist, während ein Hilfsmittel gegeben ist, um die für viele Versuche sosehr gewünschten allerhöchsten Vakua zu erhalten Mittelst eines zweiten mit Luft gefüllten Entladungsrohres, mit Seitenrohr, welches in flüssigen Wasserstoff getaucht wird, zeigt er wie man ein bestimmtes Gas, in diesem Falle Neon, im Entladungsrohr zurücklassen kann, während man das andre ganz entfernt. Will man Wasserstoff selbst aufnehmen lassen, so muss man die Absorption der Kohle benutzen. Dies wird gezeigt mit einem dritten mit Wasserstoff gefüllten Entladungsrohre, dessen Seitenrohr gefüllt ist mit Kokosnusskohle, welche durch flüssigen Wasserstoff abgekühlt wird; es wurde dann wieder ein so hohes Vakuum erreicht, dass die Entladung nicht mehr durchging.

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[1]) Die vom Redner vorgenommene Bestimmung der Isothermen hat nachher gezeigt, dass dies wohl der Fall sein kann. Vgl. Comm. N⁰. 102*a* § 5.

[2]) Man hat einen Ableiter anzubringen damit keine Funken auf den Wasserstoff überspringen.

Die Aenderung des Metallwiderstandes zeigt bei sehr tiefen Temperaturen ein Betragen, welches es wahrscheinlich macht, dass ein Minimum des Widerstandes erreicht wird, während beim absoluten Nullpunkt die Metalle vielleicht vollständig isoliren (die Einrichtung zur Untersuchung der Aenderung des Widerstandes wurde demonstrirt von Herrn CLAY). Der Redner bringt das Festfrieren der Elektronen an die Atomen, das sich hier zu offenbaren scheint, in Beziehung zu einer Zustandsgleichung der Elektronen. Die Aenderung des Widerstandes mit der Temperatur zeigt dann auch für diejenigen reinen Metalle, welche untersucht worden sind, eine merkwürdige Übereinstimmung Er demonstrirt das starke Herabsinken des Widerstandes dadurch dass er den Widerstand eines Silberdrahtes, der bei der gewöhnlichen Temperatur 30 Ohm Widerstand hat, mit einem Widerstand von 30 Ohm in einer WHEATSTONE'schen Brücke vergleicht Nach Eintauchen in flüssige Luft zeigt sich der Widerstand bis auf $^1/_4$ herabzumindern, beim Eintauchen in flüssigen Wasserstoff bis auf $^1/_{100}$.

Fester Stickstoff kann leicht mit Hilfe des im Vakuum verdampfenden Sauerstoffs (Luft) erhalten werden. Um leicht festen Sauerstoff zu bereiten braucht man flüssigen Wasserstoff. Der Redner hat einen Cylinder Sauerstoff von 1 cM. Dicke um ein gläsernes Stäbchen fest werden lassen. Derselbe wird bewahrt in einer Reagirröhre in flüssigem Wasserstoff. Zieht man den blauen Cylinder heraus, so strömt der flüssige Sauerstoff längs dem Stäbchen hinunter. Fängt man dieselbe auf in ein durchsichtiges Vakuumglas, und befreit man die Flüssigkeit vom präcipitirten Eise, dann zeigt das Spektrum die charakteristischen Absorptionsbanden des Sauerstoffs.

Der Redner zeigt dann das Schenken von Wasserstoff aus einem Glase in ein anderes, demonstrirt die geringe Dichtigkeit des Wasserstoffs und das Niederschlagen von Luft in flüssigen Wasserstoff, den man an der Luft stehen lässt, aut der Weise wie in Comm. N⁰. 94*f*.

Im kryogenen Laboratorium wird dann die Cascade bis zur flüssigen Luft in Wirkung gezeigt (Demonstration des Herrn C. A CROMMELIN) und zum Schluss werden bei den Apparaten für die Cirkulation des Wasserstoffs gezeigt das Abschenken des flüssigen Wasserstoffs aus einem Vakuumglas in eine durchsichtige doppelwandige Flasche, und endlich das Festwerden des Wasserstoffs, hauptsächlich wie angegeben in Comm. N⁰. 94*l*.

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

## Supplement No. 18*b*

## to No. 97—108.

**Dr. W. H. KEESOM.** "Die Eigenschaften von Heliumgemischen".

(*Translated from: Handelingen van het* 11$^{de}$ *Nederlandsch Natuur- en Geneeskundig Congres te Leiden,* **5 April 1907**, p. 169—174).

EDUARD IJDO — PRINTER — LEIDEN

## **Dr. W. H. KEESOM**: *Die Eigenschaften von Heliumgemischen* [1]).

Mit einem gewissen Rechte kann man nach den Untersuchungen, eingeleitet von ANDREWS und VAN DER WAALS, über die Continuität des gasförmigen und flüssigen Aggregatzustandes, behaupten, dass eine Abgrenzung dieser beiden Zustände nicht mehr möglich ist. Man wird aber in vielen Fällen, den betreffenden Sprachgebrauch behalten wollen, und man wird dann übereinkommen müssen, was man unter Flüssigkeit, was unter Gas oder Dampf zu verstehen haben wird. Die Unterscheidung der Gas- und Flüssigkeitsphase für eine einfache Substanz bei Temperaturen vom Schmelzpunkt bis zum Siedepunkt und nicht zu weit darüber bietet keine Schwierigkeit: der Flüssigkeitszustand wird charakterisirt durch kleine Zusammendrückbarkeit und Ausdehnbarkeit, der Gaszustand durch eine Zusammendrückbarkeit und eine Ausdehnbarkeit, welche ihren Ausdruck finden in den sogenannten idealen Gasgesetzen, welche von den genannten Gas- und Dampfphasen mit grosser Annäherung gefolgt werden. Bei Durchführung dieser Unterscheidung bei höheren Temperaturen, bei denen der Unterschied in Eigenschaften der beiden Phasen abnimmt, lässt man sich leiten von, was man nennen könnte, *dem Prinzip der Continuität der Phase längst der Grenzlinie* (Suppl No. 15 p. 8 Fussnote 1). Nach diesem Prinzip werden alle Phasen, welche auf der GIBBS'schen $\varepsilon$, $\eta$, $v$-Fläche für eine einfache Substanz angegeben werden durch den Zweig der Connode von den Flüssigkeitszuständen bei tiefen Temperaturen bis zum Faltenpunkt (dem kritischen Punkte der einfachen Substanz) Flüssigkeitszustände, jene, auf dem andren Zweige der Connode, von den Gaszuständen bei tiefer Temperatur bis zum Faltenpunkt, Gaszustände genannt.

Ein Fall, bei welchem dieses Prinzip bei einer einfachen Substanz besonders auf den Vordergrund kommen würde, würde vorkommen bei einer Substanz, welche sich, bei den Zuständen auf dem an der Seite der kleinen $v$'s sich ausbreitenden Flüssigkeitskamm [1]) der GIBBS'schen Fläche, in der Nähe des Faltenpunktes, associiren würde zu zusammengestellten Molekülen, welche ein grösseres Volumen haben, wie die zusammenstellenden Moleküle zusammen. [2])

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[1]) Vortrag gehalten im physikalischen Institut vor der Abteilung Physik des 11ten Congresses Niederländischer Naturforscher und Aerzte zu Leiden, 5 April 1907.

Der Flüssigkeitskamm erhebt sich dann in die Richtung der negativen $\varepsilon$'s und verschiebt sich in die Richtung der positiven $v$'s. Demzufolge würde man Coexistenz haben können zweier Phasen, von denen diejenige, welche angegeben wird durch einen Punkt auf dem von den Flüssigkeitsphasen bei tieferer Temperatur kommenden Zweig der Connode, das grösste spezifische Volumen, also die geringste Dichte haben würde.

Obiges Prinzip giebt an, dass wir diese Phase demungeachtet Flüssigkeitsphase nennen müssen, sodass also in diesem Falle die Flüssigkeitsphase leichter sein würde wie die Gasphase.

Bei einer solchen Substanz würde der kritische Punkt nicht isothermisch mittelst Kompression oder Ausdehnung aus dem homogenen Zustand erreichbar sein, wohl aber isometrisch, aber dann bei Erwärmung statt Abkühlung, wie bei den nicht associirenden Substanzen. Die $p\,T$-Kurve der gesättigten Dampfdrücke würde eine Maximaltemperatur zeigen müssen. Diese Phänomenen sind aber bei einer einfachen Substanz noch nicht gefunden worden; es giebt sogar keine Anweisung, welche die Existenz einer Substanz, bei der etwas derartiges zu erwarten sein würde, wahrscheinlich macht; dennoch kann auch kein Grund dafür angegeben werden, dass dieses nicht möglich sei.

Was aber für eine einfache Substanz nur als eine theoretische Möglichkeit betrachtet werden kann, das Sinken einer, durch Kompression schwerer gewordene Gasphase in eine Flüssigkeitsphase, ist durch ein Experiment von Prof. KAMERLINGH ONNES [3]), für binäre Mischungen, namentlich für jene von Helium und Wasserstoff, verwirklicht worden. Man wird dies in Folge der Theorie der $\psi$-Fläche von VAN DER WAALS für binäre Mischungen u. a. erwarten müssen, wenn die $\psi$-Fläche für die Gewichtseinheit der Mischungen (welche Quantität wir hier immer ins Auge fassen werden, um so mittelst des Volumens jedesmahl gleich die Dichte beurteilen zu können) eine, von der Seite $x = 0$ nach der Linie der Grenzvolumina $v = b$ schief überlaufende Falte hat, auf der keine Dreiphasengleichgewichte auftreten, und ausserdem das Grenzvolumen der flüchtigsten Komponente kleiner ist als das der anderen Komponente: $b_{22} < b_{11}$ (vergl. Suppl. No. 16). Dann wird ja die Linie welche die Berührungspunkte der zweifachen Berührungsebene, welche nach der Theorie von VAN DER WAALS auf der $\psi$-Fläche die coexistirenden Phasen kennen lehrt, verbindet, die Connodetangente, an der Seite der kleinen $x$ einen kleinen Winkel mit der $v$-Achse, in der Nähe von $v = b$ hingegen einen stumpfen Winkel mit jener Achse einschliessen. Dazwischen liegt dann irgendwo eine Connodetangente, welche mit der $v$-Achse einen rechten Winkel einschliesst und welche also Punkte auf der Connode verbindet, welche Phasen vorstellen, welche gleiches Volumen und also gleiche Dichte haben (siehe Suppl. No. 16 fig 4 und 5).

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[1]) Vergl. Comm. N°. 66.

[2]) Eine derartige Voraussetzung ist von VAN LAAR eingeführt worden, um die Ausdehnung des Wassers unter 4° und beim Gefrieren zu erklären.

[3]) H. KAMERLINGH ONNES, Comm. N°. 96*a*.

Diese Tangente, deren Ueberschreiten zur Folge hat, dass zwei coexistirende Phasen unter dem Einfluss der Schwerkraft ihren Platz wechseln (sinken und wieder aufsteigen der Gasphase in die Flüssigkeitsphase), wird barotropische Tangente, das genannte Phänomen, das barotropische Phänomen genannt. Auch bei höherer Temperatur, bei welcher die oben genannte schief auf die andere Seite sich begebende Falte entweder die Seite $x = 0$ oder die Seite $v = b$ loslässt, oder sich teilt in zwei Falten, wird eine barotropische Tangente auftreten können.

Bei einem der von Prof. KAMERLINGH ONNES angestellten Versuche, wurde ein Gemisch von Wasserstoff mit etwa 15 % Helium, mittelst eines, besonders für das Komprimiren kostspieliger Gase eingerichteten Kompressors, komprimirt in einem Glasrohr, welches in flüssigen Wasserstoff eingetaucht war. Dabei schied sich eine wasserstoffreiche Flüssigkeit ab, welche von dem sich daoben befindlichen Dampf mit einem deutlichen, nach oben konkaven Meniskus, getrennt blieb. Bei weiterer Kompression sah man bei 49 atm. die Gasphase in der Form einer unten etwas stärker gekrümmten eiförmigen Blase, welche ungefähr $^1/_7$ der Höhe des Rohres einnahm, hinunter sinken. Hiernach ist die sich unten befindende Phase von einem nach oben konvexen Meniskus begrenzt.

Giebt das Prinzip der Continuität der Phase längst der Connode an, dass wir ungeachtet der grösseren Dichte die nach unten gesunkene Phase Gasphase nennen müssen, das Experiment lehrte, dass diese Phase, was betrifft die Volumenänderungen bei weiterer Kompression und bei Ausdehnung, auch in Eigenschaften mit einer Gasphase übereinstimmt. Nach herabmindern des Druckes bis zu 32 Atm. stieg die Gasblase wieder durch die Flüssigkeitsphase jetzt aber als eine oben am meisten gekrümmte Blase auf[1]).

Berechnungen in Folge dieses Experimentes veranlassten zu einigen Betrachtungen [2]), von denen mir ein kurzer Bericht erlaubt sei. Der oben beschriebene Versuch lehrt uns, aus der als bekannt zu betrachtenden Dichte der wasserstoffreichen Flüssigkeitsphase (bei Analyse zeigte diese ungefähr 3 % Helium zu enthalten), die Dichte der heliumreichen (nach Analyse ungefähr 20 % Wasserstoff enthaltende) Gasphase bei etwa 40 Atm. und die Temperatur des unter 1 Atm. Druck siedenden Wasserstoffs kennen Stellt man behufs einer ersten Schätzung die Zustandsgleichung von VAN DER WAALS mit nicht von $v$ und $T$ abhängigen $a$ und $b$ auf die heliumreiche Phase anwendbar, so erhält man aus der Dichte eine Beziehung zwischen $a$ und $b$ für das Gemisch Entnimmt man den Bestimmungen des Reibungskoeffizienten, Wärmeleitungskoeffizienten oder des Brechungsvermögens, eine Schätzung für $b$ für Helium, so wird man zum Vermuten geführt, dass für Helium $a$, also die Anziehung zwischen den Molekülen äusserst gering sein wird. Hieraus ergiebt sich dann wieder, dass die kritische Temperatur des Heliums äusserst tief sein wird. Bei bestimmten Voraussetzungen [3]) führte die Berechnung zu einer absoluten kritischen Temperatur von Helium von etwa $^1/_3{}^\circ$ [1]).

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[1]) Der Unterschied in Druck beim Sinken und wieder Aufsteigen der Gasphase lässt sich erklären aus dem Unterschied in Dichte, welcher nötig ist um den Unterschied in Kapillarspannung der zwei verschieden gekrümmten Oberflächen überwinden zu können (Comm. N⁰. 96*b* § 4).

[2]) H. KAMERLINGH ONNES und W H. KEESOM. Comm. N⁰. 96 *b* und *c* und Suppl. N⁰. 15.

[3]) Einige dieser Voraussetzungen können nur als eine rohe Annäherung gelten. Bei den wenigen und dann noch sehr ungewissen Daten für Helium, ist aber nichts anders als eine rohe Schätzung möglich. Jedoch kann eine derartige Schätzung, bei der grossen Schwierigkeit der Versuche, welche uns mehr von dem thermodynamischen Benehmen dieses Stoffes kennen lehren werden, von grosser Bedeutung sein als Leitfaden für das Anstellen der Versuche. Die genannte Schätzung wird weiter insofern noch vom Expe-

Die also gebildete Vermutung, dass die Molekülen des Heliums nur eine äusserst geringe Anziehung ausüben, veranlasste eine Untersuchung der Eigenschaften, welche in Folge der Theorie von VAN DER WAALS erwartet werden müssen bei binären Mischungen von denen eine Komponente ein anziehungsloses oder anziehungsschwaches Gas ist. Dabei hat man gefunden, dass bei einem sehr kleinen Wert der gegenseitigen Anziehung der Moleküle der beiden Komponenten, sich mit sinkender Temperatur eine von der Seite der kleinen Volumen kommende Falte auf der $\psi$-Fläche entwickelt, welche Falte bei der kritischen Temperatur der am wenigsten flüchtigen Komponente mit der Seite $x = 0$ in Berührung kommt und dann übergeht in eine von der Linie $v = b$ nach der Seite $x = 0$ schief überlaufende Falte.

Wenn man für zwei coexistirenden Phasen, gehörend zu einer derartigen von der Seite der kleinen $v$'s kommenden, nach der Seite der grossen $v$'s geschlossenen Falte, für eine Temperatur höher als die kritische der am wenigsten flüchtigen Komponente, die reduzirten Temperaturen berechnet, findet man für beide Phasen Werte, welche bedeutend über 1 liegen können. Beide Phasen werden in Eigenschaften mit einer komprimirten Gasphase übereinstimmen. Man wird dann beide Phasen Gasphasen nennen müssen und also reden von beschränkter Mischbarkeit im Gaszustand [2]). Eine Falte welche Coexistenz zweier Gasphasen veranlasst, kann Gas-gasfalte genannt werden.

---

riment, wenigstens heute, nicht widersprochen, dass nach OLSZEWSKI das Helium durch Ausdehnung von höherem Druck gebracht auf eine Temperatur von 1°.7 absolut, noch keine Anweisung von Verflüssigung gezeigt haben würde.

[1]) Spätere Berechnungen, Suppl. N°. 16, p. 4, Fusznote 4, ergaben 1°. Für den Einfluss dieses Umstandes auf die Betrachtungen dieser Mitteilung siehe ebenda. Neue Schätzungen welche sich auf die Isothermenbestimmungen von Helium gründeten, und welche einen bedeutend höheren Wert ergeben, siehe Comm. No. 102*a* § 5.

[2]) Wenn die Fussn. 1 genannten neueren Schätzungen sich verwirklichen, und man deshalb den Heliummolekülen eine grössere Anziehung zuschreiben muss als in Suppl. No. 15 und 16 angenommen wurde, so wird man aus dem in Comm. No. 96*a* beschriebenen barotropischen Experiment folgern (vergl. Comm. No. 96*c* p. 23 Fussn. 1), entweder dass die gegenseitige Anziehung von

Die Theorie lehrt dass beim System Helium-Wasser das Verhältniss der Anziehungen und der Molekularvolumen am günstigsten ist um dieses Benehmen zu erwarten.

Ist die gegenseitige Anziehung nicht äusserst klein, aber doch noch sehr klein, so wird eine von der Linie $v = b$ kommende Falte bei ihrer Ausbreitung bei herabsinkender Temperatur nicht die Seite $x = 0$ erreichen, sondern sich durch einen homogenen Doppelfaltenpunkt mit einer von $x = 0$ kommenden Falte vereinigen. Auch dann kann Anlass bestehen, die von $v = b$ kommende Falte Gas-gasfalte zu nennen und würde Coexistenz zweier Gasphasen auftreten können. In diesem Falle würden die nötigen Drücke wahrscheinlich sehr hoch werden. Beispiele für diesen Fall werden wahrscheinlich leichter gefunden werden können, wie für den zuerstgenannten. Als Systeme welche ein derartiges Benehmen zeigen könnten, ergeben sich u. a. Helium-Stickstoffoxyd oder Helium-Ammoniak, vielleicht Helium-Neon [1]).

Entfernen diese Betrachtungen, was die beschränkte Mischbarkeit im Gaszustand anbetrifft, sich auch vielleicht all zu weit von der experimentellen Basis, um es wagen zu können ein begründetes Vermuten auszusprechen ob diese Phänomenen sich verwirklichen werden oder nicht, dies zeigt sich wohl daraus, dass die experimentelle Untersuchung der Heliumgemische uns, was das thermodynamische Benehmen von Gemischen einfach zusammengestellter Substanzen anbetrifft, noch viel wird lehren können, und dass dabei vielleicht noch sehr interessante, und bis vor kurzem nicht erwartete Erscheinungen auftreten können.

---

Helium- und Wasserstoffmolekülen relativ desto kleiner sein wird, oder dass $b_{\mathrm{He}}$ bei 20° und 40 Atm. grösser ist als angenommen wurde (vergl. Suppl. No. 16 p. 4 Fussn. 4) Im ersten Fall sind sowohl die Annahme grösserer Anziehung der Heliummolekülen aufeinander, als die kleinerer gegenseitiger Anziehung von Heliummolekülen mit denen anderer Stoffe, für die Erscheinungen von beschränkter Mischbarkeit im Gaszustand günstig (vergl. Suppl. No. 15 § 1). Im zweiten Fall wird der in anderer Richtung wirkende Einfluss des alsdann grösser werdenden $a_{12\mathrm{M}}$ aufgehoben durch den günstigen Einfluss des grösseren $b_{\mathrm{He}}$ (vergl. Suppl. No. 16 p. 4 Fussn. 4).

[1]) Vergl. aber p. 15 Fussn. 2 und Suppl. No. 16 p. 4 Fussn. 4.

# COMMUNICATIONS

FROM THE

# PHYSICAL LABORATORY

AT THE

# UNIVERSITY OF LEIDEN

BY

PROF. DR. H. KAMERLINGH ONNES,

*Director of the Laboratory.*

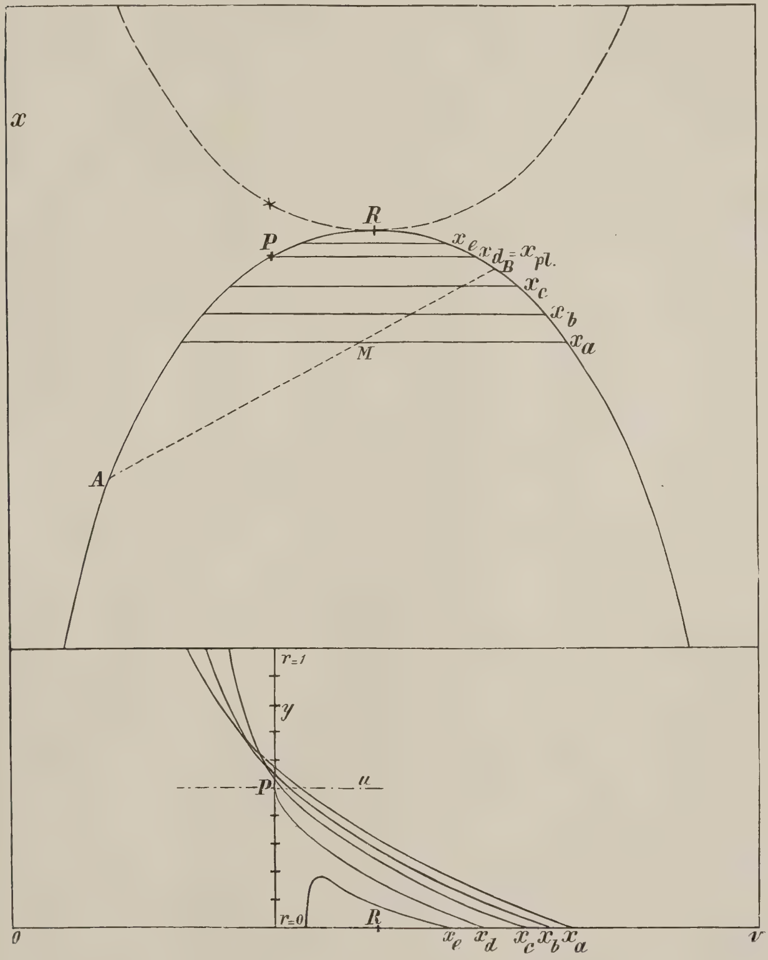
## Supplement No. 19
## to No. 97—108.

CORRIGENDA AND ADDENDA. *(With three plates).*

**May 1908.**

EDUARD IJDO — PRINTER — LEIDEN.

**Dr. J. E. VERSCHAFFELT.** "Contributions to the knowledge of VAN DER WAALS's $\psi$-surface. VII. The equation of state and the $\psi$-surface in the immediate neighbourhood of the critical state for binary mixtures with a small proportion of one of the components." **PLATE II.**



Addendum to Communication No. 81.

(Supplement No. 19 Plate I).

Dr. W. H. LATE III.

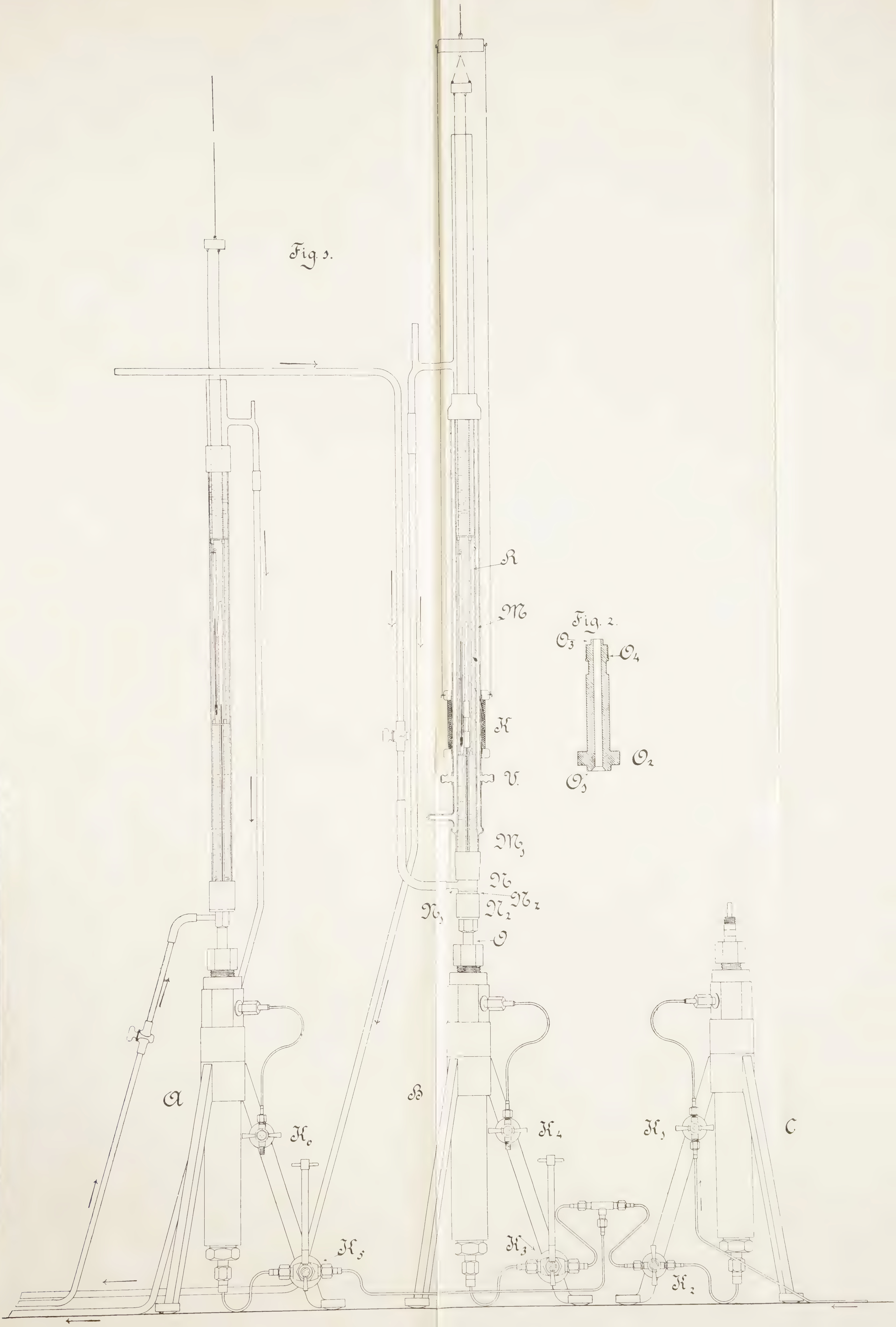


Fig. 1.

Fig. 2.

Addendum to Communication N°. 88.
(Supplement N°. 19 Plate II).

Dr. J. E. VERSCHAFFELT. "Contributions to the knowledge of VAN D WAALS's ψ-surface.

. On the possibility of predicting the properties of mixtures from th of the components."

PLATE II.

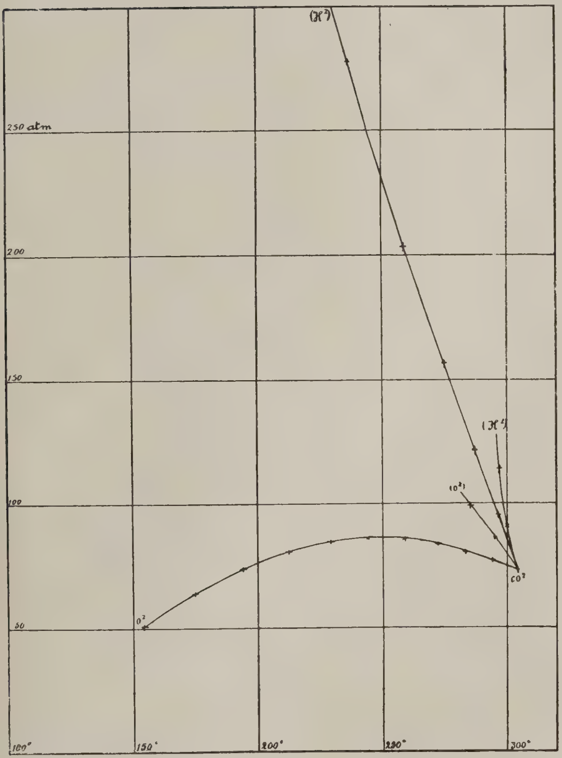


Fig. 3a.

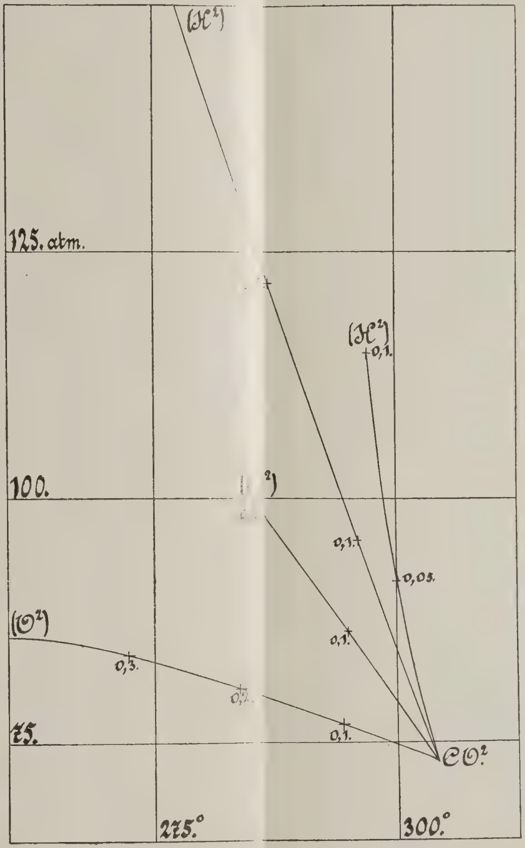


Fig. 3b.

Addendum to Supplement N°. 11
(Supplement N°. 19 **Plate III**).

[illegible]

# CORRIGENDA AND ADDENDA.

The translation of some communications in the Archives Néerlandaises has drawn the attention to the desirability of several corrigenda and addenda which with some others are united in this supplement.

## Errata Communication No. 26.

p. 4 in the figure for *P* read *F*.

„ 19 l. 8 from the top for 3.26 read 3.36.

## Erratum Communication No. 31.

titlepage l. 3 and 2 from the bottom for "Tho dispersion of the magnetic rotation in oxygen" read "Measurements on the magnetic rotatory dispersion in gases."

## Erratum Communication No. 33.

p. 14 in form. (5) for 24 read 2 *k*.

## Erratum Contents No. 25 –36.

p. VI l. 3 and 4 from the top for "The dispersion of the magnetic rotation in oxygen" read "Measurements on the magnetic rotatory dispersion in gases."

## Addenda to Communication No. 43.

§ 8. p. 12– 14 add:

The following table contains the direct experimental results:

| Temperature. | Pressure in atm. | $x$ | $x'$ | *log V.* | *log V'* |
|---|---|---|---|---|---|
| 9.1 | 3 52 | 0 | 0 | 7 4096—10 | 9.2219—10 |
| $9.4^5$ | 4.83 | 0.0088 | 0.1985 | 3991 | 9.1711 |
| 8.8 | 5.50 | 0394 | 3162 | 4178 | 9.1195 |
| 9.4 | 6 26 | 0562 | 4118 | 4162 | 9.0795 |
| $9.4^5$ | 12.37 | 2006 | 7087 | 4189 | 8.8456 |
| 9.5 | 13.51 | 2336 | 7204 | 4108 | 8.7633 |
| $9.5^5$ | 13 77 | 2506 | 7529 | 4019 | 8.7726 |
| $9\ 4^5$ | 18.64 | 3700 | 7882 | 3863 | 8 6605 |
| 9.5 | 24.55 | 5172 | 8649 | 3768 | 8.5450 |
| $9.4^5$ | 32.30 | 7431 | 9260 | 4109 | 8.3721 |
| $9\ 5^5$ | 33.01 | 0.7445 | 0.9337 | 4093 | 8,3730 |
| 9.7 | 43.86 | 1 | 1 | 7.3858—10 | 8.1622—10 |

The unit of pressure which has served for drawing fig 5 p. 12 is equivalent to 0.966 atm.

For the data of the coexisting phases at 9.5° C. deduced from the curves of fig. 5 and 6, see Comm. N⁰. 79 p. 6 footnote 2.

As a control for the pressure measurements it may be remarked that the values I found for the vapour pressure of the pure substances agree with those observed by other experimenters. So I found for $CO_2$ at 9°.7 C. 43.86 atm, whereas by interpolation I deduced from the data published by AMAGAT for the same temperature 43.9.

For methyl chloride I found at 9°.1 C. $p = 3.52$ atm., whereas the observations of REGNAULT would yield 3.42 atm.

## Addenda to Communication No. 45.

p. 4. After l. 14 from the top add:

For obtaining the mixtures, I filled the reservoir $E$ with such quantities of the two components, that the sum of the pressures was nearly 1 atm. [1]; the partial pressure of the hydrogen, expressed in atm., was then to the first approximation equal to the molecular proportion of that gas in the mixture.

For an exact calculation it was necessary to take into account the deviations from the ideal gas laws, especially from the law of AVOGADRO. Be $p_1$ and $p_2$ the pressures exerted by the quantities of hydrogen and carbon dioxide if they fill separately the same reservoir $E$ at the same temperature. These pressures are not rigorously proportional to the molecular quantities. In order to find values which are proportional to the molecular quantities, I suppose that the causes which produce the deviations from the ideal gas laws disappear; if the volume is not changed, the new pressures are the values we require. If we represent by $p$ the pressure really exerted by the gas and by $p'$ the theoretical pressure (according to the ideal gas laws) which corresponds to the same volume $v$, we may write, making use of the equation of state of VAN DER WAALS:

$$\left(p + \frac{a}{v^2}\right) \quad (v - b) = p'v$$

---

[1] As the difference of level of the mercury in the two limbs of the manometer $D$ was measured accurately to 0.1 mm., the compositions were known accurately to 3 decimals; the fourth decimal is only known approximately.

and if we put $p' = p\ (1 + e)$, to the first approximation for very great volumes

$$e = \frac{a - b\ (1 + \alpha\, t)}{(1 + \alpha\, t)^2}\, p, \quad ^{1)}$$

where for the rest we may put $x$ (or $1 - x$) instead of $p$.

p. 13 l. 15 from the bottom add the following footnote:

2) As regards fig. 2 the same remark holds as to fig. 1 (cf. p. 10 footnote 1); in particular the volumes are to be multiplied by 1.1207.

## Addenda to Communication No. 47.

p. 14 l. 2 from the top add the following footnote:

0) With the values of $a$ and $b$ given in footnote 1 to the addendum to Comm. No. 45 p. 4 (this page) we find that for hydrogen the theoretical normal volume is obtained from the normal volume by multiplying by 0.99940; for carbon dioxide we then find for that factor 1.0070 The modification caused by this in the measurement of the volumes of the latter gas is greater than the uncertainty alluded to in footnote 1 to the addendum to Comm. No. 45. p. 4 mentioned above.

p 15 l. 11 from the bottom add the following footnote:

1) It is to be foreseen here that reality lies between both (as will be seen in Suppl. No. 13 p. 5 this is really the case); but the largest difference between the formula used here and that which would express a linear variation of $\alpha_p$, which difference would correspond to $x = \frac{1}{2}$, would give an error of no more than $^1/_{4000}$ only, if the reduction is effected from 20° to 0°; so the possible error may be considered negligible.

p. 8 l. 7 from the top add:

As Prof. Kamerlingh Onnes remarked, it is not impossible that the branch of the plaitpoint curve starting from $CO_2$ rises

---

1) In the original calculations I have taken for hydrogen $e = -0.000690\, p_1$ conform to the formula mentioned p. 7, and for carbon dioxide $e = 0.0053\, p_2$, as results from the densities of hydrogen and of carbon dioxide determined by Regnault. I have repeated the calculations taking for hydrogen $a = 0.00033$ and $b = 0.00093$ after Schalkwijk (Comm. N°. 70), and for carbon dioxide $a = 0.0165$ and $b = 0.0095$, resulting from the empiric equation of state of Prof. Kamerlingh Onnes (Comm. N°. 71); the difference found, however, only affected the 4th decimal, which is uncertain.

to infinity, so that the plaitpoint curve should consist of two branches which both go to infinity [1]).

## Erratum Communication No. 59a.

p. 22 Fig. 3. vide Suppl. No. 14 p. 7 footnote.

## Addendum to Communication No. 60.

p. 27 footnote 1) add:

We afterwards noted that LALA, Ann. de Toulouse 5 G (1891) p 30 footnote 2, had already called attention to this correction.

## Erratum Communication No. 70.

p. 20. The more accurate values of $\alpha'$, $\beta'$, $\gamma'$, we communicated on a former occasion (Comm. No. 78 p. 22) yield $a = 0.00032^7$, $b = 0.00092^8$ (cf. Thesis for the Doctoıate p. 119)

## Errata Communication No. 71.

p. 6 l 2 from the top: after "unit" insert "of volume".
to footnote 2 add:

This means that volume which the considered quantity of gas would occupy if it was first at 0° C. infinitely expanded and then again, but now following the law of ideal gases compressed to 760 mm., or that for different substances such volumes are taken as units of $v$ that filled by these substances in the ideal gaseous state at 0° C and 760 mm. they would contain quantities of weight proportional to the molecular weight of them.

p 7 l. 6 from the bottom: after "this" add: "expressed in the theoretical normal volume".

p. 8 equation (4): for $\frac{C_0}{v_N}$ read $\frac{C_0}{v_N^2}$.

## Erratum Communication No. 74.

p. 5 in the table read $\Theta = 22412$.

---

[1] In Suppl. No. 11 § 10 (this Suppl. p. 18) we shall see that after the hypotheses mentioned there this really is to be expected.

## Addendum to Communication No. 75.

p. 7 footnote 1) add:

The same thesis was already proved by M. PLANCK Wied. Ann. 15 (1882) p. 457 (cf. THIESEN ZS. f. comprim. und flüssige Gase 1 (1897) p 87).

## Errata and Addenda to Communication No. 81.

p. 3 l. 10 from the bottom for $\mathfrak{o}$ read $\mathfrak{v}$.

p. 7 l. 5 add: on which, to a first approximation,

$$\frac{d^2 p}{d v^2} = - 2 \frac{k_{01} k_{30}}{k_{11}}.$$

p. 8 l. 7 for "$P_{xk}$" read "$p_{xk}$".

form. (16) and p. 27 form. (63) add the following footnote:

3) For the results of later more accurate calculations see p. 20, addendum to Suppl. No. 13 p. 8.

p. 11 l. 1 only $m_{01} > 0$ and $m_{01} < 0$ are to be placed at the head of the second and third columns of the table.

p. 13 to form. (20) the following note is to be added:

See Supplement No. 12.

p. 14 to form. (25) the following note is to be added:

The expression between brackets may be written $\frac{1}{2}(x_2 + x_1)$; it is consequently always positive, when we only consider real mixtures. As $\Phi$ is also an essentially positive quantity, we see that the sign of $\xi$ only depends from $m_{01}$. In concequence, if $m_{01} > 0$, the gaseous phase contains the largest proportion of the additional component in the mixture, and if $m_{01} < 0$ we have just the contrary. We will consequently in general have $m_{01} > 0$ when the additional component is the most volatile one.

p. 18 form. (32) and (34) must be written:

$$\Phi' = \frac{1}{m_{30}} \left[ \frac{1}{3} . \frac{m^3_{01}}{R^2 T^2} - \frac{1}{3} m_{21} + \frac{2 m_{40}}{5 m_{30}} \left( \frac{m^2_{01}}{RT} + m_{11} \right) \right] x +$$

$$+ \frac{1}{m_{30}} \left[ \frac{1}{3} m_{21} - \frac{2}{5} \frac{m_{11} m_{40}}{m_{30}} \right] x_{Tk}.$$

$$\pi' = - \frac{m^2_{01}}{R T_k} \Phi' x.$$

Addendum to § 8:

### *The projection of the isobars.*

The system of the isobars (for the equation of that system, see Suppl. No. 7, p. 6) is similar to a system of isotherms, with the point $x_{Tk}$, $v_{Tk}$ as critical point. There is, however, this difference, that in the case of the isotherms $\left(\frac{\partial^3 p}{\partial v^3}\right)_k$ is always negative; for the system of isobars, on the contrary, the corresponding expression $\left(\frac{\partial^3 x}{\partial v^3}\right)_{T_k} = -6\,\frac{m_{30}}{m_{01}}$ may become positive. There is consequently more variability in the configuration of the system of isobars than in that of the isotherms; I shall, however, not examine the different cases which may occur.

If we consider the isobar $p_{Tpl}$ we find at the plaitpoint, according to formulae (27) and (28):

$$\left(\frac{d^2 x}{d v^2}\right)_{pl} = \frac{m_{11}}{RT_k}\, x_{Tk} = \frac{m_{01}^2 + R\,T_k\, m_{11}}{R^2\, T_k^2}\, x_{Tpl.}$$

Comparing this expression with form. (37), we see that they have the same sign, when the plaitpoint is real ($x_{Tpl} > 0$); thus the connodal line and the isobar going through the plaitpoint are curved in the same direction. Moreover, as the curvature of the connodal line is finite, and that of the isobar infinitely small, the isobar envelops the connodal, in agreement with a general rule given by VAN DER WAALS [1]).

### *The spinodal line.*

The equation of this curve, which separates the elliptically curved part of the $\psi$-surface from the hyperbolically curved one, is

$$\frac{\partial^2 \psi}{\partial x^2} \cdot \frac{\partial^2 \psi}{\partial v^2} - \left(\frac{\partial^2 \psi}{\partial x\, \partial v}\right)^2 = 0.$$

Substituting for $\psi$ its expression (20) (see also Suppl. No. 12), we find, to the first approximation, that this curve is a parabola of the second degree, going through the plaitpoint, and on which:

$$\frac{d^2 x}{d v^2} = -\,\frac{6\,R\,T_k\, m_{30}}{m_{01}^2 + RT_k\, m_{11}}.$$

---

[1]) Proc. Kon. Akad. Amsterdam, 1896.

Comparing this expression with the formula (37), we see that the spinodal line is curved in the same direction as the connodal line, and its curvature is thrice as great, as shown by Korteweg [1]) in a general way.

*The curve of the maxima and minima of pressure.*

The points where the isotherms of the mixtures reach a maximum or minimum of pressure, that is to say where the lines parallel to the $v$-axis ($x =$ const.) are tangent to the isobars [2]), are situated on a curve determined by $\left(\frac{\partial p}{\partial v}\right)_x = 0$ or $\left(\frac{\partial^2 \psi}{\partial v^2}\right)_x = 0$ To a first approximation it is a parabola of the second degree, the top of which is the point $(x_{Tk}, v_{Tk})$ and on which

$$\frac{d^2 x}{d v^2} = -6 \frac{m_{30}}{m_{11}}.$$

It intersects the $v$-axis in the same points as the spinodal line, but is not always curved in the same direction. Its curvature is always negative (the concavity downwards), while that of the spinodal line, on which

$$\frac{d^2 x}{d v^2} = -6 \frac{m_{30}}{m_{11}} \frac{x_{Tpl}}{x_{Tk}},$$

is either negative or positive, according as $x_{Tpl}$ and $x_{Tk}$ have the same sign or opposite signs.

p. 20 l. 1 in form. (40) read $(m^2_{01} + RT_k m_{11})$

3 for (61) read (41).

At the head of the table in the middle of the page put $m_{01} > 0$ above the second column and $m_{01} < 0$ above the third.

p. 21 l 4 from the bottom: read

$$\Phi^2 = \frac{m_{11}}{m_{30}} x_{Tk} + K (p_1 - p_{Tk})^2 + K^1 (p_1 - p_{Tk})\, x_{Tk}.$$

p. 22 l. 7 to $p_c$ the term $-\frac{1}{2} \frac{K^1}{K} x_{Tk}$ must be added, and to $v_c$

---

[1]) Wien. Ber., 98, 1160, 1889.

[2]) In these points the isobars reach a maximum or a minimum of $x$.

the term:

$$\frac{1}{6\, m_{30}\, m_{01}} \frac{K^1}{K} \left(\frac{m_{01}\, m_{11}}{RT_k} + m_{21}\right) x_{Tk}.$$

l. 9 for $p_{Tk}$ read $p_c$.

to the part: "With respect ...... in Φ." substitute: "With respect to this centre the equation of the border curve is:

$$\left[v - v_c + \frac{1}{3\, m_{30}} \left(\frac{m_{01}\, m_{11}}{RT_k} + m_{21}\right) \frac{p - p_c}{m_{01}}\right]^2 - K(p - p_c)^2$$

$$= \frac{m_{11}}{m_{30}}\, x_{Tk} = -\frac{k_{11}}{k_{30}} (T - T_k).$$

As for the connodal line, its equation may be obtained from that of the border curve by substituting

$$x - x_c \text{ for } \frac{p - p_c}{m_{01}};\ x_c = x_{Tk} - \frac{1}{2} \frac{K^1}{m_{01}\, K} x_{Tk}."$$

p. 23 l. 1 for $x_{Tk}$ read $x_c$.

l. 2 for $p_{Tk}$ read $p_c$.

p. 24 form. (45) and (48) must be written

$$\Phi'' = \frac{m^2_{01}}{RT_k\, k_{30}} \left[\frac{1}{3} \frac{m_{01}}{RT_k} + \frac{2}{5} \frac{k_{40}}{k_{30}}\right] x -$$

$$- \frac{1}{k_{30}} \left[\frac{1}{3} k_{21} - \frac{2}{5} \frac{k_{11}\, k_{40}}{k_{30}}\right] (T - T_{xk}).$$

$$\pi'' = -\frac{m^2_{01}}{RT_k} \Phi'' x$$

and form. (46) may be simplified:

$$\Phi''^2 = -\frac{m^2_{01}}{RT_k\, k_{30}}\, x - \frac{k_{11}}{k_{30}} (T - T_{xk})$$

p. 25 form. (43), what must be read (53), is to be written:

$$\Phi''' = \frac{m^2_{01}}{RT_k\, k_{30}} \left[\frac{1}{3} \frac{m_{01}}{RT_k} + \frac{2}{5} \frac{k_{40}}{k_{30}} - \frac{1}{2} \frac{k_{11}}{k_{01}}\right] x -$$

$$- \frac{1}{k_{01}\, k_{30}} \left[\frac{1}{3} k_{21} - \frac{2}{5} \frac{k_{11}\, k_{40}}{k_{30}}\right] (p - p_{xk})$$

and the form. (51) and (54) may be simplier written thus:

$$v_{xr} = v_{xk} + \frac{m^2{}_{01}}{3\,RT_k\,k_{30}}\left(\frac{m_{01}}{RT_k} + \frac{k_{21}}{k_{11}}\right) x.$$

$$\phi'''^{2} = -\frac{m^2{}_{01}}{RT_k\,k_{30}}\,x - \frac{k_{11}}{k_{01}\,k_{30}}\,(p - p_{xk}).$$

p. 26 form. (56) may be simplified:

$$v_{xm} = v_{xk} + \frac{m^2{}_{01}}{RT_k\,k_{30}}\left[\frac{1}{3}\,\frac{m_{01}}{RT_k} - \frac{1}{2}\,\frac{k_{11}}{k_{01}} + \frac{1}{3}\,\frac{k_{21}}{k_{11}}\right] x.$$

p. 27 form (61) may also be simplified:

$$v_{xpl} = v_{xk} - \frac{m^2{}_{01}}{RT_k\,k_{30}}\left[\frac{1}{6}\,\frac{m_{01}}{RT_k} + \frac{1}{2}\,\frac{m_{11}}{m_{01}} - \frac{1}{3}\,\frac{k_{21}}{k_{11}}\right] x.$$

p. 29 conditions 2 and 3 must be permuted.

p. 32 Addendum to § 12:

It is known that, when a mixture $M$ separates in two phases $A$ and $B$ (see Pl. II)[1], the ratio of the molecular quantities of the two phases is equal to the ratio of the segments $AM$ and $MB$ of the nodal line; that is to say, if we consider a gram-molecule of the mixture, the points $A$ and $B$ representing respectively the liquid and the gaseous phase, the liquid phase contains $\frac{BM}{AB}$ gr.mol. of the mixture, and the gaseous one $\frac{AM}{AB}$ gr. mol. The ratio $r = \frac{BM}{AB}$ is the very one we consider when describing the rate of the condensation[2].

---

[1] This figure gives a schematical representation of the condensation; it is enlarged infinitely in the direction of the volumes. I have drawn two connodal curves, a plain and a dotted one, curved in opposed directions; for both the condensation phenomena are the same. At the base of the figure it is shown how the molecular quantity $r$ of the liquid varies with the total volume of the mixture. Holding the figure upright, we see the rate of the condensation in the case of a retrograde condensation of the first kind ($v_{Tr} > v_{Tpl}$). Taking it upside down we have the case of a retrograde condensation of the second kind ($v_{Tr} < v_{Tpl}$).

[2] The variation of the volume of the liquid phase is evidently what we observe directly. As, however, the total variation of volume is infinitely small in our considerations, the variations of the ratio of the liquid volume to the total volume being, at the contrary, finite, the ratio of the molecular quantities is, in first approximation, equal to the ratio of the volumes. In consiquence, the figure represents also the variation of the volume of the liquid phase. (It should also be compared with fig. 2 of the plate to Comm. No. 45 and with plate II to Comm. No. 88).

Now

$$r = \frac{v_2 - v}{v_2 - v_1} = \frac{v_{Tk} + \Phi + \phi - v}{2\,\phi} = \frac{1}{2} - \frac{v - v_{Tk} - \Phi}{2\,\phi}. \qquad (\alpha)$$

I shall put $y = r - \frac{1}{2}$ and $v - v_{Tpl} = z$, and suppose that the difference between $x$ and $x_{Tpl}$ is infinitely small in comparison with $x_{Tpl}$ itself, so that $x - x_{Tpl}$ is of the same order as $x_{Tpl} - x_{Tr}$, that is of the second order. Putting for $\phi$ its expression (form. 23), and eliminating $p$ by means of the equation (68), we may write:

$$y = \frac{-z}{2\sqrt{-\frac{m_{01}^2 + RT_k\, m_{11}}{RT_k\, m_{30}}\left[(x - x_{Tpl}) - \frac{m_{01}}{RT_k}\, x_{Tpl}\, z\right]}} \qquad (\beta)$$

In fact $y$ may not exceed the limits $+\,{}^1/_2$ and $-\,{}^1/_2$; but mathematically we can imagine $y$ taking values higher than the first limit and lower than the second[1]. As for $z$ it remains always infinitely small of the first order[2]. We may, however, render the schematical representation finitely large in the direction of the $v$-axis by introducing the new variable $u = \frac{z}{x_{Tpl}}$; equation ($\beta$) becomes then:

$$y = \frac{-u}{\sqrt{-\frac{m_{01}^2 + RT_k\, m_{11}}{RT_k\, m_{30}}\left(\frac{x - x_{Tpl}}{x^2_{Tpl}} - \frac{m_{01}}{RT_k}\, u\right)}},$$

what may also be written:

$$y = \frac{-u}{\sqrt{\frac{m_{01}^2\,(m_{01}^2 + RT_k\, m_{11})^2}{R^4\; T_k^4\, m_{30}^2}\left\{\frac{2\, x_{Tpl}}{v_{Tr} - v_{Tpl}}\, u - \frac{x - x_{Tpl}}{x_{Tr} - x_{Tpl}}\right\}}} \qquad (\gamma)$$

In this form, the equation shows that the rate of the condensation only depends from the relative values of $x_{Tr}$ and $x_{Tpl}$ on one hand, and of $v_{Tr}$ and $v_{Tpl}$ on the other hand. First, the denominator being essentially positive, $y$ and $u$ have different signs, that is to say the condensation curve is situated in the second and fourth quadrants. It has a vertical asymptote with the abscissa:

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[1] $y > \frac{1}{2}$ would signify that the liquid volume is greater than the total volume, $y < \frac{1}{2}$ would mean a negative liquid volume.

[2] Of the same order as $v_{Tpl} - v_{Tr}$.

$$u = \frac{1}{2} \frac{v_{Tr} - v_{Tpl}}{x_{Tpl}(x_{Tr} - x_{Tpl})} (x - x_{Tpl})\,;^{1)}$$

if $v_{Tr} > v_{Tpl}$ the asymptote is placed either at the right or at the left of the origin (plaitpoint-volume) according as $x - x_{Tpl}$ and $x_{Tr} - x_{Tpl}$ have the same sign or opposite signs; and, for $v_{Tr} < v_{Tpl}$ this rule must be reversed. As the quantity under the rootsign must remain positive, the condensation curve must always be placed to the right of the asymptote, when $v_{Tr} > v_{Tpl}$, and to the left when $v_{Tr} < v_{Tpl}$. For values of $x$ not enclosed between $x_{Tr}$ and $x_{Tpl}$, $u$ may become zero and pass from a positive value to a negative one; at the same time $y$ changes its signs in the other sense. For values of $x$ enclosed between $x_{Tpl}$ and $x_{Tr}$, $u$ never changes its sign during the condensation; it reaches a maximum or a minimum value (retrograde condensation); if $v_{Tr} > v_{Tpl}$, $u$ remains positive and $y$ negative (r. c. of the first kind); if $v_{Tr} < v_{Tpl}$, $u$ is always negative and $y$ positive (r. c. of the second kind). The existence of an asymptote renders the rate of the retrograde condensation unsymmetrical: a liquid phase disappears more rapidly than it appears, and a gaseous phase appears more rapidly than it vanishes. [2])

For a mixture the molecular proportion of which is precisely that which corresponds to the plaitpoint ($x = x_{Tpl}$), the equation ($\gamma$) becomes

$$y = \frac{-u}{\sqrt{\dfrac{m_{01}^{2}(m_{01}^{2} + RT_k m_{11})^2}{R^4 T_k^4 m_{30}^{2}} \dfrac{2x_{\mathrm{T}pl}}{v_{Tr} - v_{Tpl}} u}}\,;$$

and this represents a vertical straight line corresponding to the

---

[1]) An infinitely great value of $y$ corresponds to $\Phi = 0$; that means: the abscissa of the asymptote is determined by the intersection of the horizontal line, corresponding to the mixture, with the tangent to the connodal line through the plaitpoint.

[2]) Comp. VAN DER WAALS. Cont. II. p. 128.

plaitpoint volume ($u = 0$, value of $y$ undetermined), and a semiparabola situated either in the second or fourth quadrant, according as $v_{Tr} <$ or $> v_{pl}$. All these circumstances agree with the figure.

## Addenda to Communication No. 88.

p. 13 l. 7 from the bottom add the following footnote:

1) In sealing care was taken that the top part of the tube got the form of a hemisphere, in order to avoid sticking of the stirrer there. For the same reason the narrow part under the divided stem, which narrow part had to prevent the stirrer from falling into the reservoir beneath, was formed by sealing there a short glass tube with the same external diameter as the stem, but a smaller internal one, so that the stirrer rested on a plane rim of glass.

p. 20 l. 1 from the top add the following footnote:

[0]) CHAPPUIS (Trav. et Mém. du Bur. Intern. des Poids et Mesures, t 13 p. 12) has drawn attention to the variation of volume to which the bulbs are subject during the calibration when the mercury exerts different pressures according to the different levels. I had already taken account of this circumstance.

p. 23 Table XII add the following footnote:

6) These experiments yield data for calculating the coëfficient $B$ in the empirical equation of state of KAMERLINGH ONNES for these mixtures (cf. Comm. No. 92 p. 18). For determining $C$ determinations of the compressibility of mixtures at higher pressures are suited, such as were performed by LALA, Ann. de la Fac. des Sciences Toulouse 5 G (1891) for mixtures of carbon dioxide and air, carbon dioxide and hydrogen, and oxygen and hydrogen between 100 and 1000 cm of mercury. For determining the coëfficients $D$ etc., and so studying the deviations of the law of corresponding states measurements at still higher pressures are better suited, such as are treated here in chapter V (cf. MATHIAS, Journ. de phys. (4) 4 (1905) p. 48).

p. 30 to § 2 add:

The arrangement of the pressure cylinders with manometer and piezometer has been drawn in Plate III fig 1 Plate III fig. 2 represents the steel flange for placing the experimental tube in the pressure cylinder. The rim $O_1$ fits closely into the inner cylindrical part of the pressure cylinder and serves for preventing the leather washer which procures perfect closure between $O_2$ and the corresponding rim of the pressure cylinder, from being pressed away laterally [1]; the rim $O_3$ is intended to prevent the leather washer which serves to close the waterjacket of constant temperature when it is screwed on $O_4$, from being pressed against the glass, and so to distort the piezometer stem when the jacket is screwed off.

p. 40 to footnote 2) add:

See also Pl. III fig. 1.

p. 54 footnote 1 l. 5 from the bottom, after "densities" add:

(Cf YOUNG, Proc Phys. Soc. London, 1894/95, p. 648).

p. 62 l. 4 from the bottom add:

Cf. also VAN DER WAALS, Verh. Kon. Akad. Amsterdam 1880, p. 23, Contin. I p. 155.

p. 71 l. 3 from the top, add the following footnote:

1) According to the data obtained by VERSCHAFFELT for mixtures of carbon dioxide and hydrogen (cf. p. 20, addendum to Suppl. No. 13) $v_{xk}$ also for these mixtures shows a maximum; there, however, the maximum does not fall in the region examined experimentally (cf. also BRINKMAN, Thesis for the Doctorate, Amsterdam 1904, p. 74).

p. 73 l. 12 from the bottom add the following footnote:

1) VAN DER WAALS, Proc Kon. Akad.v.Wet. Amsterdam, Sept. 1905, has compared the results of my experiments with relations he deduced for the plaitpoint curve in the neighbourhood of one of the components, while applying his equation of state. In order to obtain a satisfactory agreement for the quantities he considers, VAN DER WAALS was induced to suppose that $b$ varies with the volume in such a way as corresponds to what researches about pure substances had taught. So the hypothesis from which I started that to the first approximation mixtures follow the law of corresponding states, is found confirmed by those considerations.

As was anticipated by VAN DER WAALS l. c p. 279, the fact that the agreement he found between the quantities $\left(\frac{\partial p}{\partial x}\right)_v$ as they were deduced from the data of the plaitpoints, of the points of contact, or of the critical points of the homogeneous mixtures, was not as good as the agreement I found here, must be mainly attributed to this circumstance, that VAN DER WAALS founded his comparison on the quantities $\frac{\Delta T_{xpl}}{\Delta x}$ etc, $\Delta x$ being 0.1047 or 0.1995. Indeed if we calculate with the aid of the formula's of VAN DER WAALS l.c. $\left(\frac{\partial p}{\partial x}\right)_{vT}$ for $x = 0$, $T = T_k$, $v = v_k$, making use of the quantities $\left(\frac{d T_{xpl}}{dx}\right)_{x=0}$ etc. deduced here, the agreement becomes satisfactory.

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[1] This precaution has been introduced by HARTMAN.

## Erratum Communication No. 92.

p. 12 l. 1 from the top: for "first" read "second".

## Errata Communication No. 95a.

p. 16 l. 6 from the bottom: for — [212. 832] read — 212. 868.
l. 5 from the bottom: for — 212. 868 read — [212 832].
p. 22 l. 8 from the bottom: for [— 212. 832] read — 212. 868.
for + 58 read + 52.
l. 7 from the bottom: for — 212 868 read [— 212. 832].
for + 38 read + 44.

## Errata Communication No. 95c.

p. 42 l. 15 from the bottom: for 50 920 read 59.920.
l. 7 „ „ „ : for [— 212. 83] read [— 212.87].
l. 6 „ „ „ : for — 212. 87 read — 212. 83.

## Erratum Communication No. 95d.

p. 49 l. 5 from the bottom: for *inflecion* read *inflection.*

## Erratum Communication No. 96c.

p. 24 Table I in the heading read $M_2/M_1 = 2$.

## Erratum Communication No. 97a.

p. 16 l. 12 from the top: for $\left[\frac{dp\,v_A}{dt}\right]_{t'}^{t}$ read $\left[\frac{dp\,v_A}{dt}\right]_{t'}^{t''}$

p. 21 l 6 from the bottom: for 46.419 read 46.491.

## Errata Communication No 97b.

Title page: to the title should be added: XV. Influence of the deviation from the law of BOYLE-CHARLES on the temperature, measured with the scale of the gas-thermometer of constant volume according to the observations with this apparatus.

p. 34 form. (3): between the second and third terms of the numerator placed between ( ), a — sign should be placed.
p. 35 l. 12 from the top: for **VII.** H$_2$. 1 read **VII.** H$_2$. 2.
p. 36 table XVI and p. 38 table XVII: see Comm. No. 102*d*.
p. 40 form. (6) for $B_{t'_2}^{(p)} H_T^2$ read $B_{t'_2}^{(p)} H_T$.
l. 2 from the bottom for though read through.
p. 41. For chapter XV see Comm. 102*d*.
p. 43 l. 13 from the top for pression-coefficient read pressure-coefficient.

### Erratum Communication No. 98.

p. 13 l. 12 from the top, for wich read which.
p. 19 l. 18 from the top: for crritical read critical,
p. 20 l. 4 from the bottom: for wiht read with.

### Erratum Supplement No. 99b.

p. 11 Table IV column 3: for 21,999 read 21,899.

### Erratum Communication No. 99c.

p. 22 Table I column $Au_{\rm VI}$: for 0.16822 read 0.25234.

### Errata Supplement No. 6.

p. 14 l. 18 from the top: for $\mathfrak{p}_{21}-27.76082$ read $\mathfrak{p}_{21}=27.76082$.
p. 16 l. 2 from the bottom read:

$$\rho = \frac{1}{v_k} \mp \frac{\Phi}{{v_k}^2} + \frac{1}{{v_k}^2}\left(\frac{\Phi^2}{v_k} - \Phi.\right)$$

### Errata Supplement No. 7.

p. 5 to form. (2) add the note: „See supplement N$^0$. 12".
l. 4 from the bottom, for $k_{01}\,\alpha\,T_k$ read $k_{01}\,\alpha'\,T_k$.

### Addenda to Supplement No. 8.

p. 7. to the table add the following footnote:

3) For the coefficients VI 2 see Comm. N$^0$. 92 p. 17.

l. 4 from the bottom add the following footnote:

4) Since a system of coefficients VII. 1 has been calculated (cf. Comm. N$^0$. 97*a*, p. 24 footnote 1), taking for the absolute temperature of 0° C. the

more exact value 273.°09, and also correcting the critical data. This set has been obtained by combining the observations concerning hydrogen, oxygen, nitrogen and ether of AMAGAT with those concerning ether of RAMSAY and YOUNG and those concerning isopentane of YOUNG.

Reduced virial coefficients VII. 1.

| | |
|---|---|
| $10^8\ \mathfrak{B}$ | $157\,9500\,t - 305.7713 - 231.8247\frac{1}{t} - 97.5686\frac{1}{t^3} - 4.2530\frac{1}{t^5}$ |
| $10^{11}\ \mathfrak{C}$ | $66.5702\,t - 66.6723 + 145.2913\frac{1}{t} + 79.0260\frac{1}{t^3} + 25.0946\frac{1}{t^5}$ |
| $10^{18}\ \mathfrak{D}$ | $434.680\ t - 131.462 - 903.004\frac{1}{t} + 367.7055\frac{1}{t^3} - 178.5625\frac{1}{t^5}$ |
| $10^{25}\ \mathfrak{E}$ | $-1588.948\,t + 5725.652 - 4331.720\frac{1}{t} + 864.610\frac{1}{t^3} + 40.449\frac{1}{t^5}$ |
| $10^{32}\ \mathfrak{F}$ | $1685.000\ t - 6477.876 + 6019.629\frac{1}{t} - 1512.028\frac{1}{t^3} + 144.537\frac{1}{t^5}$ |

## Errata and Addenda to Suppl. No. 11.

p. 11 to footnote 3 add :

The fact that in some parts of the region in question rather distant from point *A* (cf. VAN LAAR, Proc. Kon Akad. Amsterdam, Sept. 1906), the plaitpoint curve is no longer continuous between the two critical points, but shows a branch which raises infinitely, evidently does by no means alter the conclusion that there is a plaitpoint temperature lower than all the others, were it the absolute zero. Such parts however do not directly belong to the mixtures of the second type of HARTMAN (loc. cit.), which I am considering here. These mixtures are to be found only in the neighbourhood of point *A*.

And to footnote 4 :

As this area is entirely situated in the region where the plaitpoint curve is discontinuous (cf. VAN LAAR loc. cit.) it does not properly correspond to the third type of HARTMAN (this type would not exist for mixtures of normal substances). The conclusion, however, concerning the existence of a maximum plaitpoint temperature is still justified in so far as the branch that raises infinitely reaches a temperature higher than all other plaitpoint temperatures.

p. 12 § 9 add the footnote :

A similar remark as has been added to footnote 3 p. 11 may be made here.

p. 12 § 10. As from calculations of Dr. KEESOM (cf. Suppl. No. 16 p. 11 footnote 1) followed that an error had been made in my calculations for the table of § 10, this § must be changed as follows, where also some remarks about mixtures of carbon dioxide and oxygen are added.

Finally, in order to show by means of a couple of examples that the suppositions whence we started enable us to find in the main accurately the course of the plaitpoint elements, I will give here the results of the calculations, executed by Dr. KEESOM for mixtures of $CO_2$ and $H_2$ and of $CO_2$ and $O_2$. For the critical elements of hydrogen the most recent data, found by OLSZEWSKI, were used: $T_k = 32.3$, $p_k = 14.2$ atm. In order to render comparison more easy, I have reproduced in the same table the observed values of the plaitpoint pressures and temperatures.

Mixtures of $CO_2$ and $H_2$.

| | Calculated. | | Observed. | |
|---|---|---|---|---|
| | $T_{xpl}$ | $p_{xpl}$ | $T_{xpl}$ | $p_{xpl}$ |
| $x = 0$ (pure $CO_2$) | 304°.5 | 72.9 atm. | 304°.5 | 72.9 atm. |
| 0.05 | | | 300.2 | 91.85 |
| 0.1 | 296.7 | 95.7 | 297.3 | 114.2 |
| 0.2 | 287.1 | 121.8 | | |
| 0.3 | 275.1 | 156.7 | | |
| 0.4 | 259.1 | 203.8 | | |
| 0.5 | 237.0 | 278.0 | | |
| 0,6 | 202.7 | 429.5 | | |
| 0.7 | 140.8 | 7686 | | |
| 0.713 | 126.1 | $\infty$ | | |

Mixtures of $CO_2$ and $O_2$.

| | Calculated. 1) | | Observed. | |
|---|---|---|---|---|
| | $T_{xpl}$ | $p_{xpl}$ | $T_{xpl}$ | $p_{xpl}$ |
| $x = 0$ (pure $CO_2$) | 304°.5 | 72.9 atm. | 304.02 | 72.93 |
| 0.1 | 294.6 | 77.1 | 295.03 | 86.60 |
| 0.2 | 283.6 | 80.7 | 285.55 | 99.65 |
| 0.3 | 272.4 | 83.9 | | |
| 0.4 | 259.2 | 85.8 | | |
| 0.5 | 244.9 | 86.2 | | |
| 0.6 | 229.6 | 85.1 | | |
| 0.7 | 212.3 | 80.9 | | |

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1) According to more accurate calculations some numbers in this table differ somewhat though not essentially (only in the last decimal) from those given in the Archives Néerlandaises (2) 13 p. 16.

| | | |
|---|---|---|
| 0.8 | 194.9 | 74.5 |
| 0.9 | 175.0 | 63.9 |
| 1 (pure $O_2$) | 154.2 | 50.7 |

Fig. 3*a* Plate II is the graphical representation of this table. Fig. 3*b* gives the part which can be compared with observations on a larger scale.

According to the foregoing, the branch of the plaitpoint curve for mixtures of $CO_2$ and $H_2$, starting from the critical point of carbonic acid, should after our hypotheses go upward to infinity. The course of the observed part of the curve agrees with this prevision [1]).

As regards the plaitpoint curve for mixtures of $CO_2$ and $O_2$, this would be continuous; the same is indicated by the curvature of the part that is observed by KEESOM.

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[1]) In consequence, the schematical representation HARTMAN (Comm. Suppl. N⁰. 3, Plate I, fig. 9) has given of this curve is exact as for the branch *d* on the $CO_2$-side, which has been drawn according to my measurements. The branch *m* however, which has been drawn without taking into account possible complications introduced by a longitudinal plait or the apparition of the solid state, has no signification.

## Addendum to Supplement No. 13.

p. 8 at the end add:

*La variation des grandeurs critiques avec la composition.*

Les formules suivantes expriment enfin comment quelques grandeurs critiques varient avec la composition, dans le voisinage de l'anhydride carbonique pur:

$$
\begin{aligned}
T_{xk} &= T_k\,(1 - 1.219\,x + 1.93\,x^2)\\
p_{xk} &= p_k\,(1 - 1.645\,x + 2.69\,x^2)\\
v_{xk} &= v_k\,(1 + 0.62\,x - 0.95\,x^2)\\
T_{xpl} &= T_k\,(1 - 0.333\,x + 0.96\,x^2)\\
p_{xpl} &= p_k\,(1 + 4.50\,x + 10.5\,x^2)\\
v_{xpl} &= v_k\,(1 - 0.40\,x - 8\,x^2).
\end{aligned}
$$

## Erratum Supplement No. 15.

p. 21 for l. 6 from the bottom read:

p. 831. See also Suppl. No. 16 p. 11.
[3]) Cf. p. 18 footnote 1.

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